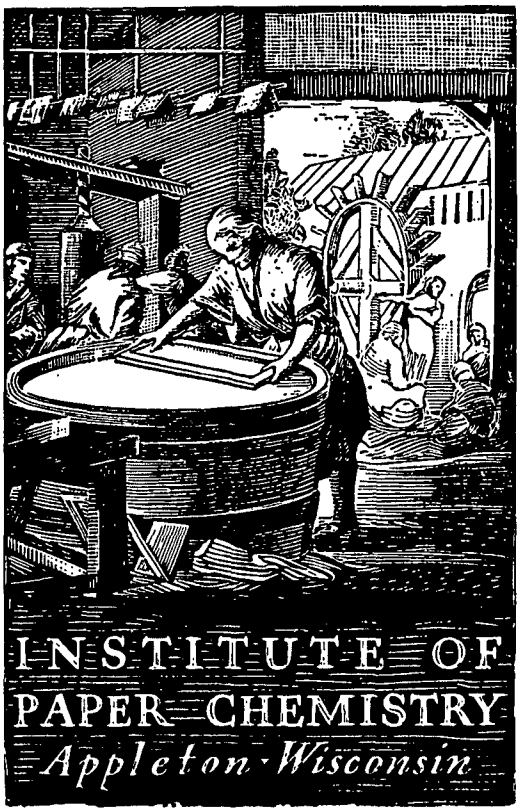


IMPROVING RETENTION OF PARTICULATE MATTER WHEN EMPLOYING RECYCLED WHITE WATER

Project 3245

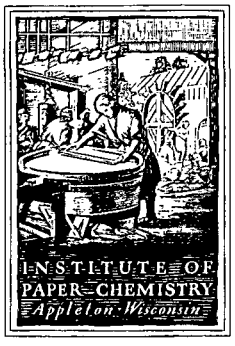
Report Two

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

March 7, 1977



THE INSTITUTE OF PAPER CHEMISTRY
Post Office Box 1039
Appleton, Wisconsin 54911
Phone: 414/734-9251

March 30, 1977

Project 3245

TO: Members of The Institute of Paper Chemistry

PROJECT 3245 - PROGRESS REPORT TWO

IMPROVING RETENTION OF PARTICULATE MATTER
WHEN EMPLOYING RECYCLED WHITE WATER

The enclosed report describes a portion of an investigation into the factors which influence retention of titanium dioxide, kaolin clay, and fiber fines in a recycled white water system. A previous progress report presented the results of studies of the role of pulp fines in retention. Progress Report Two focuses attention on the effect of hard water and sulfate ion on retention in a recycle system. Both are shown to cause lower retention. Additionally, the level of understanding of the effects of pulp fines on retention is strengthened beyond the results reported in Progress Report One by examing two new pulps.

We would be happy to answer questions you may have concerning this work. We also invite your comments, criticisms, or suggestions for improving the project.

Sincerely yours,

John W. Swanson

John W. Swanson
Director
Division of Natural
Materials & Systems

JWS/sjb
Enclosure

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

IMPROVING RETENTION OF PARTICULATE MATTER WHEN EMPLOYING RECYCLED WHITE WATER

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to

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March 7, 1977

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

IMPROVING RETENTION OF PARTICULATE MATTER WHEN EMPLOYING RECYCLED WHITE WATER

SUMMARY

The first progress report described the results of studies of the role of pulp fines on the retention and optical properties of TiO_2 and filler clay with a bleached kraft northern softwood. City water having less than 100 ppm hardness (as $CaCO_3$) and an initial pH of 8.5-9.5 was used. Pulp consistencies approaching those found in headboxes and under controlled agitation were employed to prepare handsheets from a beaten pulp and a classified pulp at various filler addition levels. The white water from the first handsheet set was recycled to make a second handsheet set. Various levels of alum were used as a retention aid.

In the case of titanium dioxide, good retention was achieved even in the absence of pulp fines. When fines are present in the system, however, the TiO_2 particles are found attached to the fines and to the fiber walls. In the latter case, particles appear to be primarily attached to fibrils protruding from the surface of the fiber. These fibrils may be thought of as fines still bound to the fiber. In the white water the titanium dioxide is attached to the fines. However, when the pigment was recycled and retained in subsequent handsheets there was no evidence of agglomeration of fines and pigment particles. In addition, the handsheets had excellent light scattering coefficients suggestive of a small average particle size. These results implied that the attachment forces between the pigment and fines in the white water must have been weak compared to the hydrodynamic shearing forces of mixing and drainage. The retention of the pigment recycled was found to be considerably lower than for the initial retention values.

In contrast to titanium dioxide, the retention of clay was found to be very sensitive to the presence of the pulp fines. Clay particles were nearly always associated with the fines, with very little being bound by the fiber surface. Even in the case of the classified pulp the little clay that was retained seemed to be on residual fines. The retention of clay on either the beaten or classified pulp was reduced significantly by increasing the agitation, suggesting that the loss mechanism is primarily a response by the clay to the hydrodynamic shear forces rather than by a loss on displaced fines. In the white water the clay was coagulated with fines or with itself. Just as in the case of the TiO_2, however, the recycled clay material retained in subsequent handsheets had excellent light scattering coefficients, suggestive of the small average particle size.

The influence of pulp fines on the retention of both titanium dioxide and clay particles illustrates the importance of optimizing the retention of pulp fines.

Work in Phase II is concerned with the mechanisms of retention loss. The objective is to identify those components of a papermaking furnish which may cause a change in retention of fines or filler material upon recycle of the white water. The emphasis during this phase of the program is on those ions common to hard waters with special attention given to the sulfate ion. In addition, the effects of a mixed filler system, composed of TiO_2 and clay, are examined. The white water has been recycled up to eight times in systems containing filler material. Finally, the level of understanding of the effects of pulp fines on retention of particulate matter is strengthened beyond the results reported in Progress Report One by examining systems of a bleached kraft northern hardwood and a northern stone groundwood.

The effect of hard water on retention is examined by preparing a series of make-up waters with varying degrees of hardness with and without sulfate ion. Water with hardness of about 150 ppm produces near maximum retention even in the absence of alum. If alum is added to this hard water system, retention may decrease as a result of the system becoming highly cationic. The magnitude of the decrease in retention would be dependent on water hardness, the greater the hardness the larger the retention decrease. At lower hardness, say less than 100 ppm, alum is beneficial. Altogether these results suggest that for a given water hardness there is a specific alum concentration which will yield optimum retention, and that alum concentration decreases as water hardness increases. However, optimum retention for either the 445 CSF pulp or the classified pulp, and for either clay or TiO_2 pigment, is seen to decrease significantly in hard water as compared to distilled water.

The effect of sulfate ion on TiO_2 retention is studied by plotting retention versus sulfate concentration at constant alum concentration. Initially an increase in retention with increasing sulfate up to about 50 ppm is observed. Thereafter retention decreases with increasing sulfate concentration. These experiments were conducted in a pH range where sulfate is able to form an inner sphere complex with aluminum ion thereby reducing the ionic charge and its effectiveness in collapsing the double layer. This interaction could explain the decrease in retention at the higher sulfate concentrations.

The retention of either TiO_2 or clay from a mixed pigment system is less than that observed from an identical papermaking furnish containing only clay or TiO_2. The presence of clay significantly reduces TiO_2 retention at low alum levels. As alum concentration increases, TiO_2 retention approaches that obtainable from a single pigment furnish. The reduction in clay retention in the presence of TiO_2,

however, remains constant over the entire range of alum concentration investigated. This is a further indication of basic differences in clay and TiO_2 retention mechanisms. The loss of TiO_2 retention in the presence of clay may be explained by agglomeration of TiO_2 with clay and subsequent loss of the more poorly retained clay. As alum concentration increases, the tendency of TiO_2 to agglomerate with clay is reduced and TiO_2 retention increases. The loss of clay retention on the other hand is not so easily visualized.

Retention data from multiple recycled white water systems are analyzed by comparison to a steady state model. The model assumes that single pass retention is constant and that in time the ash value of the sheet equals the ash added to the headbox per cycle. Theoretical curves are calculated using the mean value of single pass retention from each recycle experiment. The data points tend to fall below the theoretical curves indicating that single pass retention is not constant but decreases slightly with increasing cycle number. The same comparison indicates that in most cases 90% of the steady state ash content of the sheet is reached after 4 cycles.

Optical data obtained from recycle systems in hard water and distilled water show the same trends as reported in Progress Report One. Recycled pigment is apparently redispersed and upon subsequent retention displays an optical benefit comparable to that of material retained on the initial cycle. The TiO_2 pigment specific scattering coefficient, $\underline{S}_t$, is shown to vary with furnish loading. The value of $\underline{S}_t$ decreases as loading increases indicating that maximum optical benefit from TiO_2 is obtained at lower furnish loadings. This is not true, however, for clay where the pigment specific scattering coefficient is not affected by clay loading in the furnish.

Two new pulps, a bleached kraft northern hardwood and a groundwood pulp are introduced in the work of Phase II. Retention of clay and TiO_2 are examined with these pulps as a function of alum concentration. No recycle experiments are performed with the new pulps. The data from the new pulps corroborates the observations reported in Progress Report One regarding the role of fines in retention of TiO_2 and clay in an alum system.

INTRODUCTION

This project was created to investigate the effects of system closure on the complex interactions which occur between fibers, fines, filler material, and other wet end additives. The need for such a program has been outlined in detail in the first report (1). The objectives of the program remain the same. They are: (1) To establish the controlling phenomena affecting the retention of particulate matter, (2) to determine those major factors which cause variability in retention, and (3) to establish methods of retention control and maximization.

In brief, the program is being carried out in four phases. The role of pulp fines on the retention of recycled particulate matter was examined in Phase I and reported in the first Progress Report (Progress Report One). This report is concerned with Phase II of the program, the causes of retention loss. The remaining two phases of the program are: III, means of improving retention, and IV, factors causing variations in the optical properties, and methods of control.

The literature concerning recycling was presented in Progress Report One (PR1).

RESULTS AND DISCUSSION

EXPLANATORY REMARKS

The results are presented in two parts. That work which concerned the separate effects of furnish components and multiple recycling of the white water is included in Part I. Part II deals with investigations performed on the new pulp systems, and the format in this section is similar to that used in PR1.

Because of the diversity and number of separate experiments described in this report, an attempt has been made to cross reference those results reported in various sections. Accordingly each experiment is identified by number, and a complete listing of all experiments is included in Appendix I. In the case of multicycle data, the cycle number is included and is separated from the experiment number by a dash, e.g., 173-4 refers to cycle 4 of experiment 173.

In all of the work described herein the consistency was maintained at 0.3, the agitation at 70 cpm and the pH at 5.0 with H_2SO_4. All other variables are noted as used.

PART I: THE CAUSES OF RETENTION LOSS

THE INFLUENCE OF FURNISH COMPONENTS

The Effects of Hard Water

Table I presents the compositions of the hard waters prepared and used in this investigation. Based on data reported for a number of mills these composites are believed to be representative of actual hard waters. To investigate the role of the sulfate ion in the system, one hard water was prepared without sulfate. Unless otherwise indicated, hard water as used in the following discussion includes sulfate.

The effect of hard water (with sulfate) on the single pass retention of clay or TiO_2 in a mixed filler system is shown in Fig. 1. The mixed system contained 5% TiO_2 and 25% clay. The results are presented versus alum concentration for both pulp systems studied in PR1. For purposes of comparison, Fig. 1a and 1b also present the retention of TiO_2 and clay from the mixed filler system using distilled water, and also when 2% rosin is added to either the distilled or hard water. The effect of the mixed filler system itself on retention is described later. The method of determining the fractions of TiO_2 and clay retained from the mixed filler system is described in the Experimental Section.

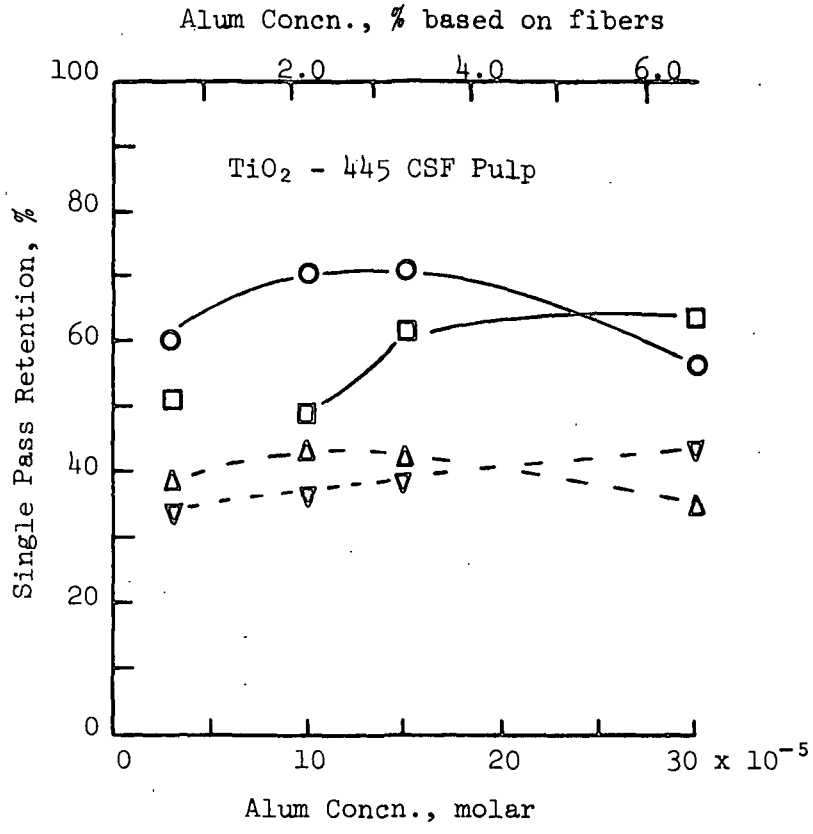
For either the 445 CSF pulp or the classified pulp, and for either the clay or TiO_2 pigment, the retention is seen to decrease significantly in the hard water system compared to the distilled water system. The effect is most evident in the 445 pulp where the retention is highest. The probable explanation for this decrease in retention with hard water is proposed later.

TABLE I

HARD WATER COMPOSITION

Salt[a]	Concentration, ppm	Ca^{+2}, ppm	Mg^{+2}, ppm	Na^{+}, ppm	SO_4^{-2}, ppm	Cl^{-}, ppm	HCO_3^{-}, ppm	Total Hardness, ppm (as $CaCO_3$)	Dissolved Solids, ppm	pH
				Hard Water						
$CaSO_4 \cdot 2 H_2O$	92	21			51					
$CaCl_2 \cdot 2 H_2O$	323-336	87-92				155-162				
$MgSO_4$	124		25		99					
$NaHCO_3$	69			19			50			
Na_2SO_4	384			124	260					
	Total	110	25	143	409	160	50	375	987	7
				Hard Water Without Sulfate						
$CaCl_2 \cdot 2 H_2O$	390-406	105-110				187-196				
$MgCl_2$	98		25			73				
$NaHCO_3$	69			19			50			
NaCl	316			124		192				
	Total	107	25	143	0	457	50	369	782	7

[a]The $CaCl_2 \cdot 2 H_2O$ used during the course of the experiments absorbed some water so the actual salt content changed some as indicated.



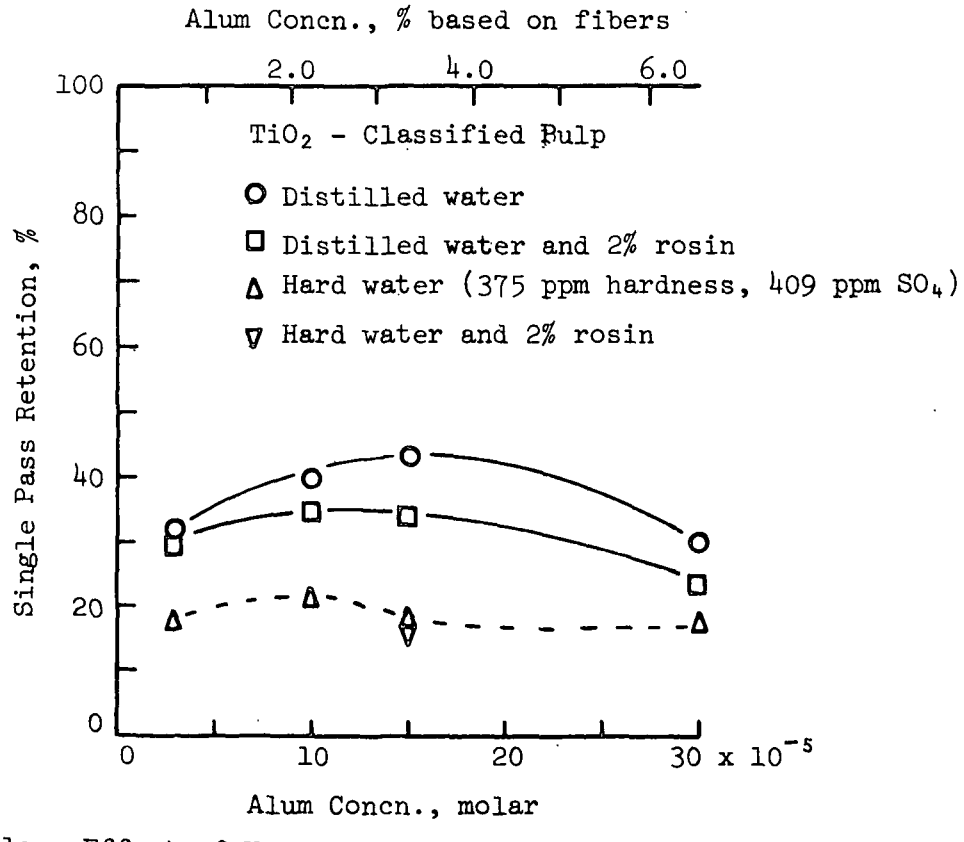
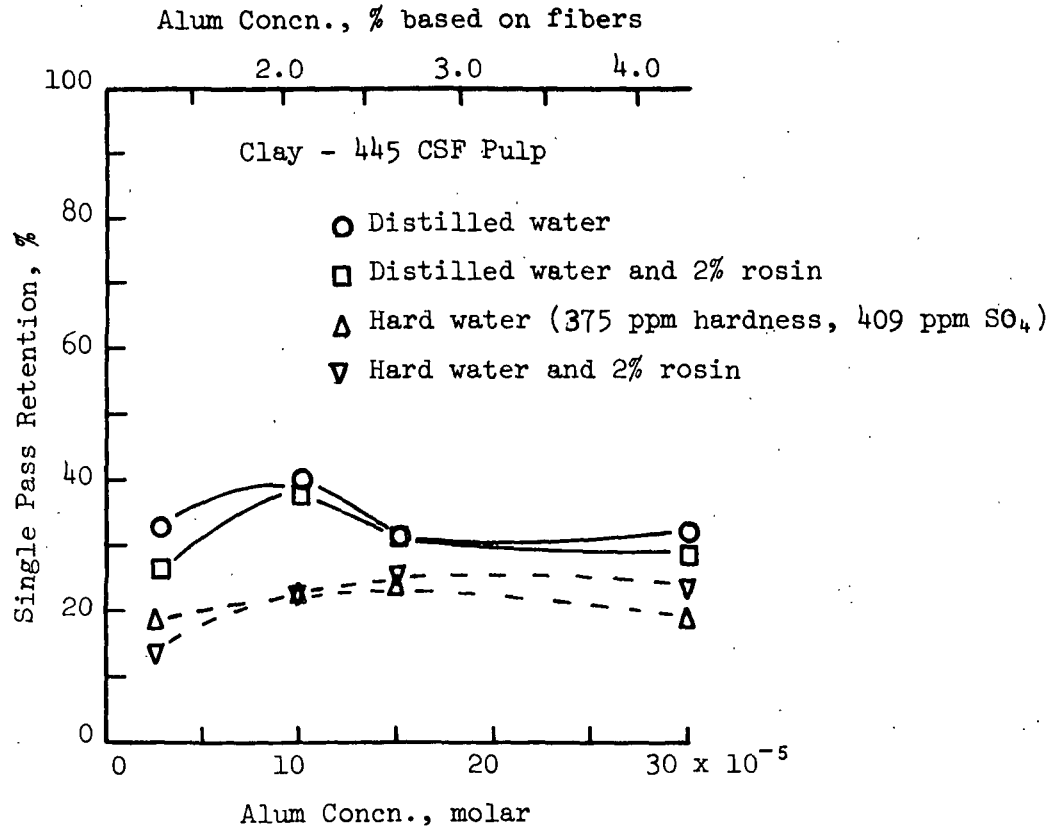


Figure 1a. Effect of Hard Water and Rosin on Retention of TiO_2, 0.3% Consistency, pH 5.0, 70 cpm, 5% TiO_2 and 25% Clay Together



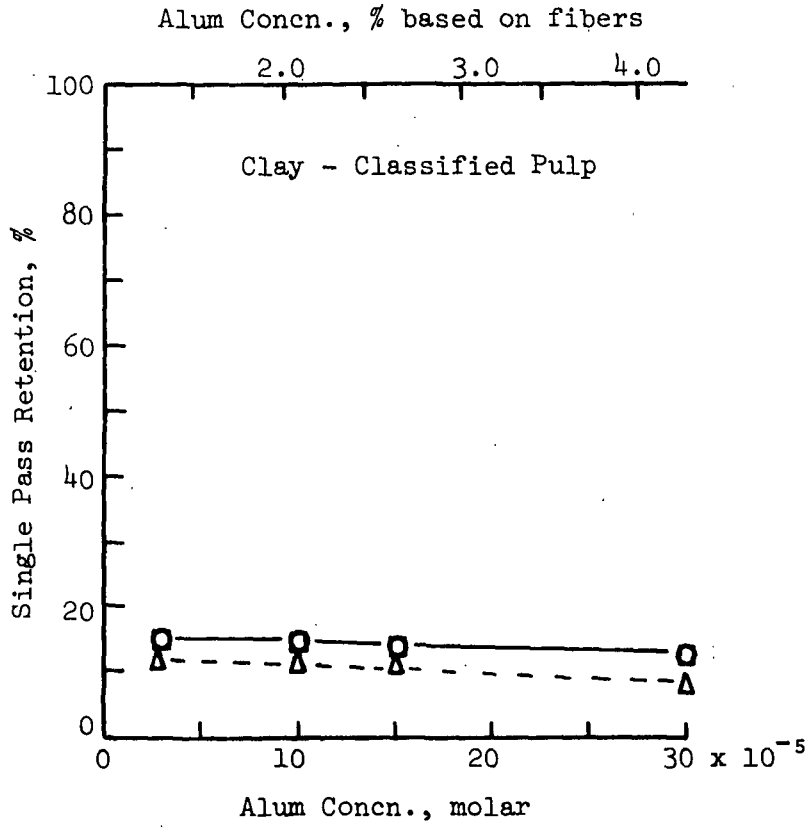


Figure 1b. Effect of Hard Water and Rosin on Retention of Clay, 0.3% Consistency, pH 5.0, 70 cpm, 5% TiO_2 and 25% Clay Together

Figure 1 also indicates that the retention of either pigment in the system prepared without rosin is a maximum around 2 to 3% alum based on fiber, consistent with the results reported in PR1. This broad maximum does not seem to be altered significantly in the hard water system.

The zeta potentials (in mV) of the suspended solids in the above systems are listed in Table II. There seems to be two effects here:

1. With a couple of exceptions the zeta potentials for the filler-free systems are less positive than those with filler regardless of alum concentration, water hardness, or presence of rosin. This would argue that the alum cations are most strongly adsorbed by the pigment than by the fines and that it is the former that is being measured.

2. The zeta potentials in hard water are less positive than the corresponding systems in distilled water. This is likely a result of sulfate ion binding by the adsorbed cationic aluminum species thereby reducing the latter's effect on the zeta potential. Moore [Tappi 56(3):71(1973] has used similar arguments to explain the utility of multivalent anions on the drainage of pulps treated with a combination of alum and cationic polyelectrolyte.

Also included in Table II are the results of pulp fines loss measurements. The results are essentially independent of water type and alum concentration. The exception is the overall trend toward greater fines loss at the highest alum levels. This latter trend may not be real but rather a result of the increased weight of aluminum adsorbed on the fines. The analysis handles all non-TiO_2 ash as if it were clay, and thus the results at the highest alum concentrations may be in error. In like manner the tendency toward greater (apparent) fines loss with rosin addition may also be a result of rosin remaining with the fines.

TABLE II

ZETA POTENTIAL AND FINES LOSS DATA FOR MIXED PIGMENT SYSTEMS

(0.3% Consistency, pH 5, 70 cpm, 5% TiO_2 + 25% clay)

Suspending Medium	Alum Addition, % based on fiber	Pigment Loading, % based on fiber	Zeta Potential of Suspended Solids, mv		Pulp Fines Loss, %	
			Whole Pulp (445 CSF)	Classified Pulp	Whole Pulp (445 CSF)	Classified Pulp
Distilled water	None	None	-18	-19	1.7 ± 0.2	0.2 ± 0.2
		TiO_2, 5; clay, 25	--	--	--	--
	0.7	None	-12	-5	1.8 ± 0.2	0.2 ± 0.2
		TiO_2, 5; clay, 25	-4	8	2.0	0.8
	2.2	None	-3	17	1.9 ± 0.2	0.2 ± 0.2
		TiO_2, 5; clay, 25	17	19	2.0	0.4
	3.3	None	-4	14	1.7	0.3
		TiO_2, 5; clay, 25	19	25	2.1	0.5
	6.7	None	5	15	2.2	0.6
		TiO_2, 5; clay, 25	14	25	2.6	0.9
Distilled water + 2% rosin	None	None	--	--	--	--
		TiO_2, 5; clay, 25	--	--	--	--
	0.7	None	-12	2	2.5	0.7
		TiO_2, 5; clay, 25	-10	6	2.7	1.2
	2.2	None	5	21	2.3	0.5
		TiO_2, 5; clay, 25	16	20	2.4	1.0
	3.3	None	5	16	2.5	0.5
		TiO_2, 5; clay, 25	17	19	2.7	0.7
	6.7	None	9 ± 1	14 ± 1	2.8 ± 0.1	1.0 ± 0.1
		TiO_2, 5; clay, 25	17	17	3.2	1.5
Hard water	None	None	--	--	--	--
		TiO_2, 5; clay, 25	--	--	--	--
	0.7	None	-4	6	1.7	0.2
		TiO_2, 5; clay, 25	-7	-6	2.4	0.8
	2.2	None	-5	6	1.9	0.3
		TiO_2, 5; clay, 25	-6	9	2.2	0.9
	3.3	None	-5	5	1.9	0.5
		TiO_2, 5; clay, 25	7	9	2.5	1.0
	6.7	None	0 ± 0.5	6 ± 1	2.3 ± 0.1	0.9 ± 0.1
		TiO_2, 5; clay, 25	7	9	2.8	1.4
Hard water + 2% rosin	None	None	--	--	--	--
		TiO_2, 5; clay, 25	--	--	--	--
	0.7	None	--	--	--	--
		TiO_2, 5; clay, 25	-5	0	2.2	--
	2.2	None	--	--	--	--
		TiO_2, 5; clay, 25	0	5	2.6	--
	3.3	None	--	--	--	--
		TiO_2, 5; clay, 25	10	7	2.8	1.6
	6.7	None	--	--	--	--
		TiO_2, 5; clay, 25	6	5	2.7	--

The effects of hard water, with and without sulfate, on retention and zeta potential were also examined on the filler materials separately. Table III provides the experimental parameters and results for both the clay and TiO_2 material for the two pulp systems. Note that all investigations were conducted at 2.2% alum based on fiber, i.e., that value at which maximum retention is (generally) obtained (see Fig. 1). Table III also includes the mixed system results in order that a direct comparison with the latter system can be made. Several trends are apparent. The retention of either filler in either water system is noted to be less from the mixed pigment system than the retention from the single pigment system. As noted earlier, the retention of clay or TiO_2 is less in the hard water systems than in the distilled water system, and there is a significant decrease in zeta potential as well. For the hard water containing no sulfate the retention values for either pigment are intermediate between the distilled water and hard water with sulfate systems. The zeta potentials are considerably more cationic for the no-sulfate system, however.

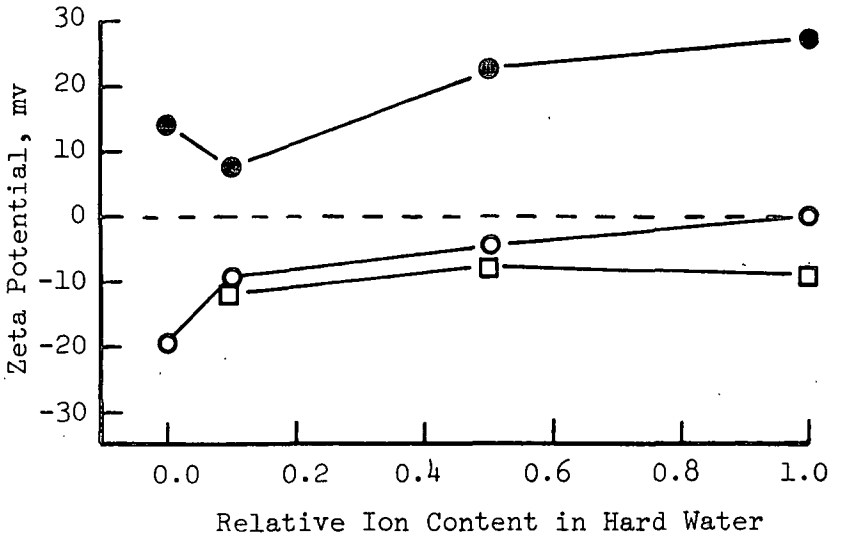
Figure 2 depicts the retention of TiO_2 for the 445 CSF pulp as a function of the water hardness. The abscissa is a relative ion content based on the maximum hard water concentrations presented in Table I. In the absence of alum the retention increases as the ion content of either hard water, with or without sulfate, increases. Retentions in hard water without alum comparable to those obained in distilled water with alum, are achieved at about 50% of the maximum hard water strength. During this same change in hard water concentration the zeta potential becomes less negative suggesting that the retention increase results from a double layer compression. The divalent cation strength at the 50% hard water concentration is about 1.5×10^{-3} molar.

TABLE III

THE RETENTION OF TiO_2 AND CLAY IN VARIOUS TYPES OF WATER

(Bleached softwood kraft, 0.3% consistency, 2.2% of alum, pH 5, 70 cpm)

Pulp	Pigment	Type of Water	Pigment Retention, %		Zeta Potential of Suspended Solids, mv	
			Alone	In Blend	Pigment Alone	In Blend
Whole (445 CSF)	TiO_2	Distilled	79	70	+14	+17
		Hard with sulfate	58 ± 1	43	+8 ± 2	+6
		Hard without sulfate	54 ± 2	--	+23 ± 4	--
	Clay	Distilled	44	39	0	+17
		Hard with sulfate	23 ± 3	23	-2 ± 3	+6
		Hard without sulfate	33 ± 2	--	+10 ± 4	--
Classified	TiO_2	Distilled	56	40	+29	+19
		Hard with sulfate	30	21	+16	+9
		Hard without sulfate	35	--	+31	--
	Clay	Distilled	18	14	+17	+19
		Hard with sulfate	--	11	--	+9
		Hard without sulfate	--	--	--	--



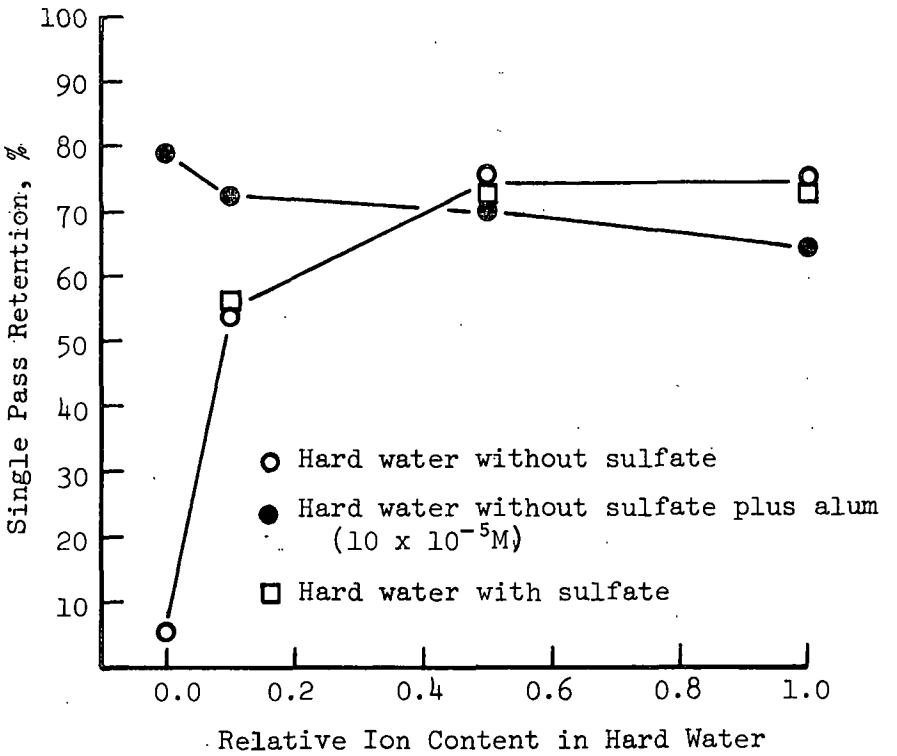


Figure 2. Effect of Water Hardness and Sulfate Ion on Zeta Potential and TiO_2 Retention

With 2.2% alum added to the system the retention is markedly improved at the lowest hard water concentrations. At values around one-half of the full hard water strength, corresponding to approximately 150 ppm hardness, the beneficial effect of the alum is lost. At higher values of hardness the presence of alum is detrimental. The addition of alum to the system prepared without sulfate ion resulted in zeta potentials which were positive over the entire range of hard water conditions.

The investigations concerning retention as it is affected by the hardness of the water may be summarized as follows. Water with hardness greater than about 150 ppm is sufficient to achieve a near maximum retention by the compression of double layers, even in the absence of alum. If alum is added to this hard water system, the retention may be decreased as a result of the system becoming highly cationic. The magnitude of the decrease in retention would be dependent on the water hardness, the greater the hardness the larger the retention decrease. At lower hardness, say less than 100 ppm, the alum is beneficial. At these lower hardnesses the zeta potentials of the suspended solids, specifically TiO_2, are positive, whereas the fiber surface or fibrils, must not be since the retention is high. Altogether these results suggest that for a given water hardness there is a specific alum concentration which will yield optimum retention, and that the alum concentration decreases as the water hardness increases. However, the optimum retention is generally less than that measured in the distilled water-alum system.

The specific absorption and scattering coefficients have been determined for the above systems. Figure 3 depicts the total specific scattering coefficient at 457 μm for the mixed filler system, plotted against the percent TiO_2 in the sheet. The hard water and distilled water results are compared at the four alum

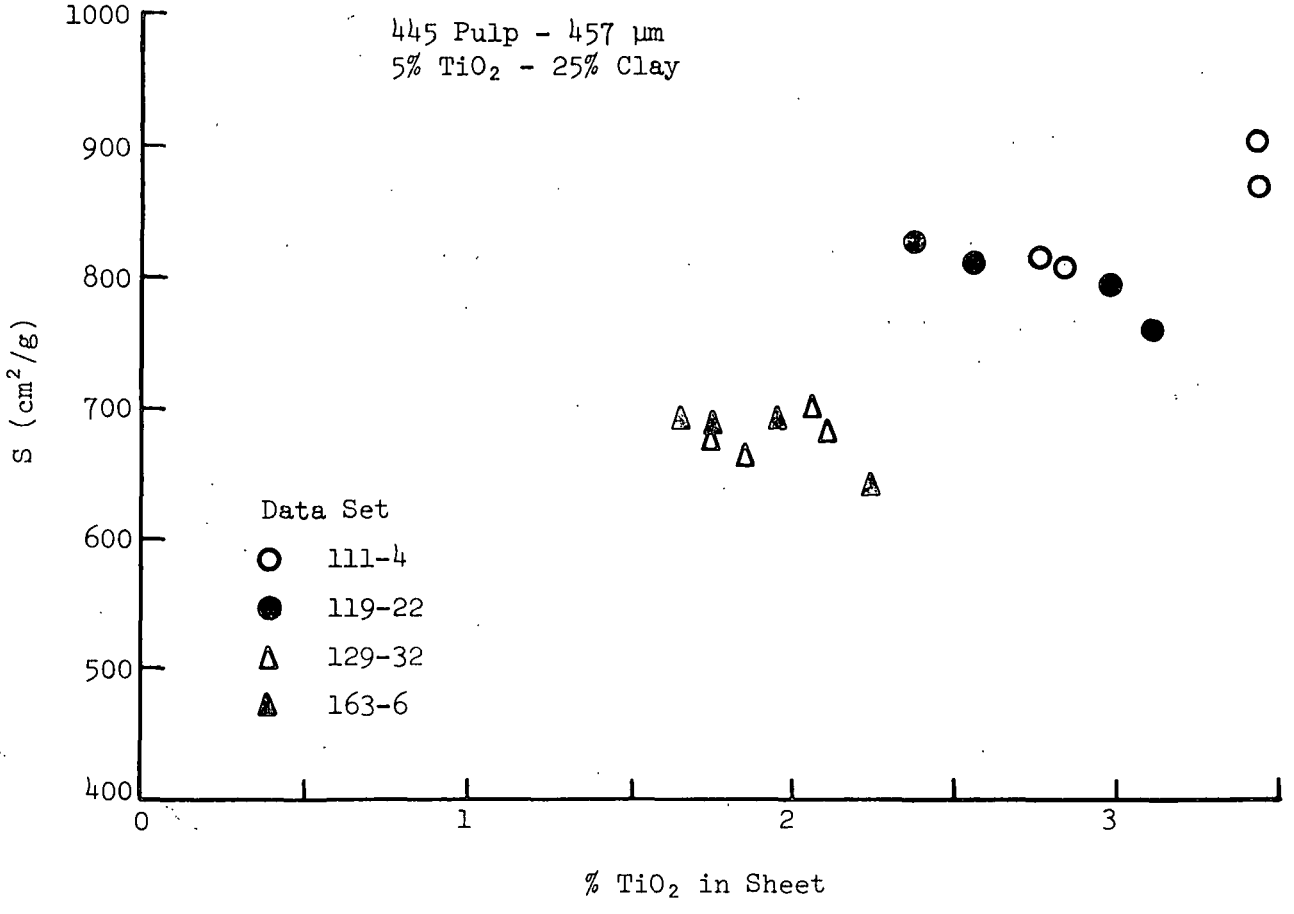


Figure 3. The Specific Scattering Coefficient *versus* Percent TiO_2 in the Sheet for a Mixed Pigment System

addition levels. From this figure no readily apparent trends are obvious except that the hard water decreases retention compared to the distilled water. Figure 4 presents the same experimental data but presents the specific scattering coefficient for the TiO_2, $\underline{S_t}$, *versus* percent TiO_2. $\underline{S_t}$ is determined from

$S = S_p \frac{W_p}{W} + S_c \frac{W_c}{W} + S_t \frac{W_t}{W}$ where the superscripts p, c, and t refer to pulp, clay and TiO_2, respectively. The $\underline{S_p}$ values are obtained separately and the value of $\underline{S_c}$ was obtained from PR1. Although there may be some question as to the validity of determining $\underline{S_t}$ in this manner, the observed trends are believed to be meaningful. Figure 4 shows that for the alum-hard water system $\underline{S_t}$ varies over a large range. The numbers correspond to the alum addition levels, Number 1 being the

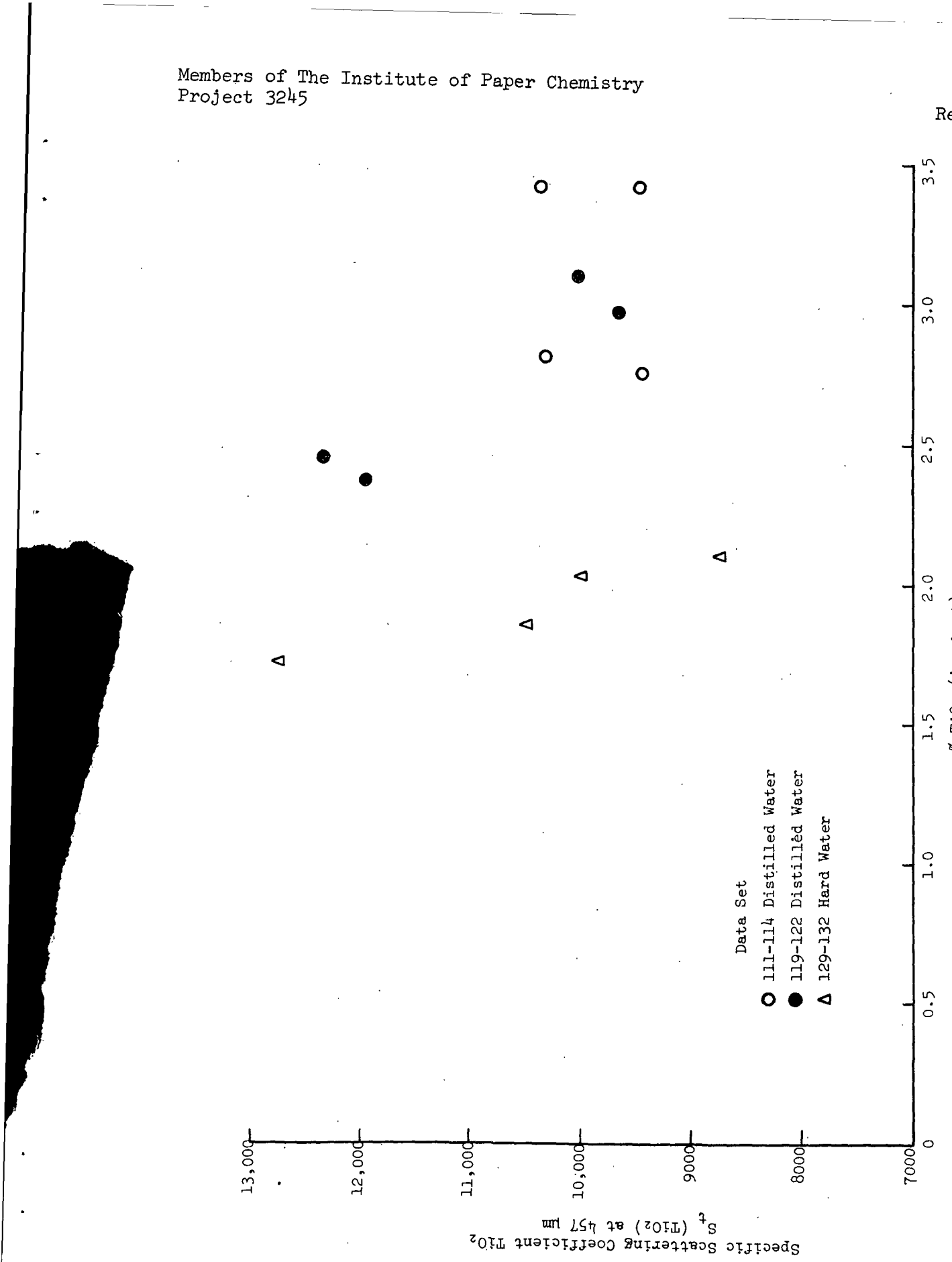


Figure 4. The TiO_2 Pigment Specific Scattering Coefficient versus % TiO_2 in the Sheet for a Mixed Pigment System

lowest. Note that at the optimum retention alum level (2) the value of S_t is a minimum. Beyond this point, as more alum is added the retention decreases and the specific scattering coefficient increases. The same effect is observed in the distilled water results although not as pronounced. An analogous trend is noted for the system containing rosin. In this case the retention increases at the higher alum levels but S_t decreases.

The hard water-alum system results suggest that self flocculation of TiO_2 is occurring at optimum retention, thus decreasing S_t by effectively increasing particle size. As the alum level increases the TiO_2 is restabilized and even though less of it may be retained, that which is provides greater optical benefit. The zeta potential results presented in Table II do not clearly speak to this trend. The zeta potential remains essentially constant and positive at the higher alum levels. We must not forget, of course, that we also have clay in this system.

The Effect of Sulfate Ion on TiO_2 Retention (Constant Cation Concentration)

Figure 5 shows the retention of TiO_2 versus sulfate concentration with 2.2% alum. The maximum sulfate concentration on the abscissa is equivalent to 4.2×10^{-3} m/l of SO_4^{-2}, not including the sulfate added with the alum. For the 2.2% alum level the SO_4^{-2} level is approximately 0.3×10^{-3} m/l. Figure 5 reveals a small initial increase in retention with increasing SO_4^{-2} up to about 0.4×10^{-3} molar SO_4 (50 ppm). Thereafter the retention decreases with increasing sulfate concentration. Over the entire range of sulfate ion concentrations investigated the zeta potential remained positive but decreased significantly as the sulfate concentration increased. The initial large decrease in zeta potential, corresponding to the initial increase in retention, is consistent with the idea of a double layer compression by the divalent ion. The maximum

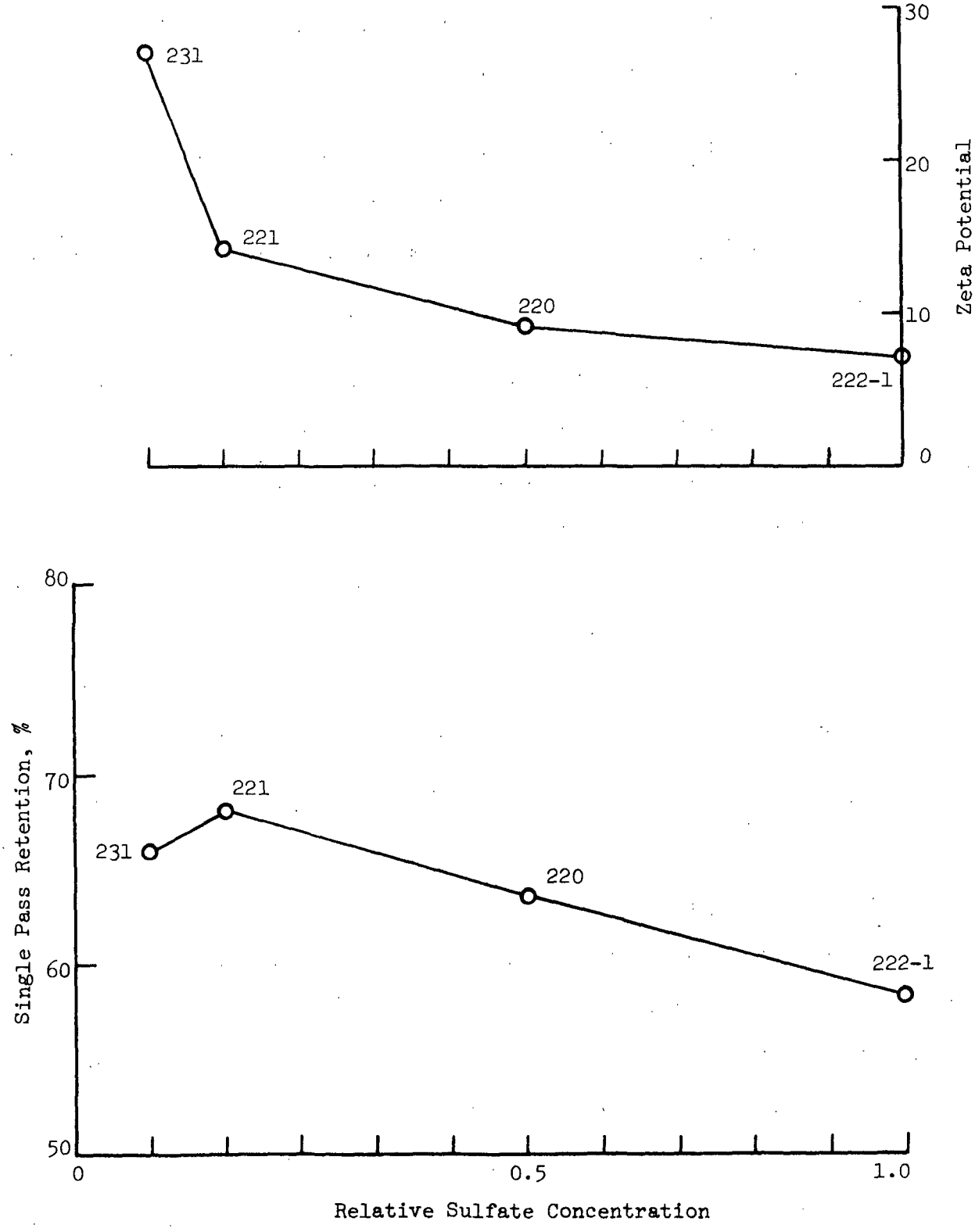


Figure 5. The Effect of Relative Sulfate Ion Concentration on TiO_2 Retention and Zeta Potential at Constant Alum Concentration

effect occurs at a total sulfate ion concentration of about 0.7×10^{-3} molar (hard water plus alum) which is about equivalent to the Kruyt value.

The decrease in retention at higher SO_4^{-2} levels parallels the decrease in zeta potential. If with increasing sulfate levels there is increased coagulation, this subsequently could lead to decreased retention via a hydrodynamic shear effect.

In conclusion it appears that increased sulfate levels, up to 50 ppm, can increase retention in a cationic system by compression of double layers. The extent of the cationic system developed would be affected by the complex of SO_4^{-2} with divalent and trivalent ions [Stryker and Matijevic (1)]. The decrease in retention at sulfate levels beyond 50 ppm appears incongruous with the idea of compression of double layers. However, divalent anions have been shown to develop bridges in polyelectrolyte systems. If divalent bridge coagulation occurs in this system, as the optical data mentioned above seem to suggest, then the observed decrease in retention can be explained. This, of course, will require further testing.

The Effect of Mixed Pigments

Alum affects the retention of TiO_2 and clay from the mixed systems in about the same manner as observed in the earlier work of Phase I. The results on the mixed filler systems are shown in Fig. 1a and 1b. The noticeable exception to the earlier trend of a maximum in the retention near 2 to 3% alum are the results for the TiO_2 retention on the 445 CSF pulp. Here the maximum retention occurs at higher alum add-on levels. There is no apparent explanation for this effect at present.

The retention of TiO_2 from the mixed system is less, at the lower alum levels, than the retention values found in Phase I for a TiO_2 pigment system only. These results are shown in Fig. 6. The solid lines are those curves shown in Fig. 1 of PR1, based on either clay or TiO_2 filler systems only. The dotted curves are the corresponding retention values at a given alum concentration when the filler material was 5% TiO_2 and 25% clay. The latter data were obtained in a distilled water system. Note that in the case of TiO_2 retention, the presence of the clay significantly reduces the retention at low alum levels. The effect is observed in either the classified or 445 CSF pulp, but appears to be more prominent in the former. As the alum concentration increases, the results from the mixed and separate systems for TiO_2 converge.

A similar behavior is observed for the retention of clay from the mixed system. That is, the presence of the TiO_2 in some way interferes with the clay retention, as compared to a clay only system. The major difference observed in the latter system is that the reduction in retention appears quite uniform over the entire range of alum concentrations for both pulps.

A possible explanation for the reduction in TiO_2 retention by the clay may be deduced by considering the zeta potential of the clay particles at the low alum concentration range. With respect to the classified pulp system, the appropriate data is presented in Fig. 4 of PR1. It is shown in this figure that at 5% TiO_2 and 25% clay loadings (separately), at less than 1% alum levels, the zeta potential of the TiO_2 is positive while the clay is negative. The rapid development of a cationic charge by TiO_2 at low alum levels, where the clay is still anionic, has also been observed by McKenzie (2) and Chen (3). It seems possible then, that in this alum range, the cationic pigment coagulates with the anionic surfaces, which in this case are fiber and clay. Since the

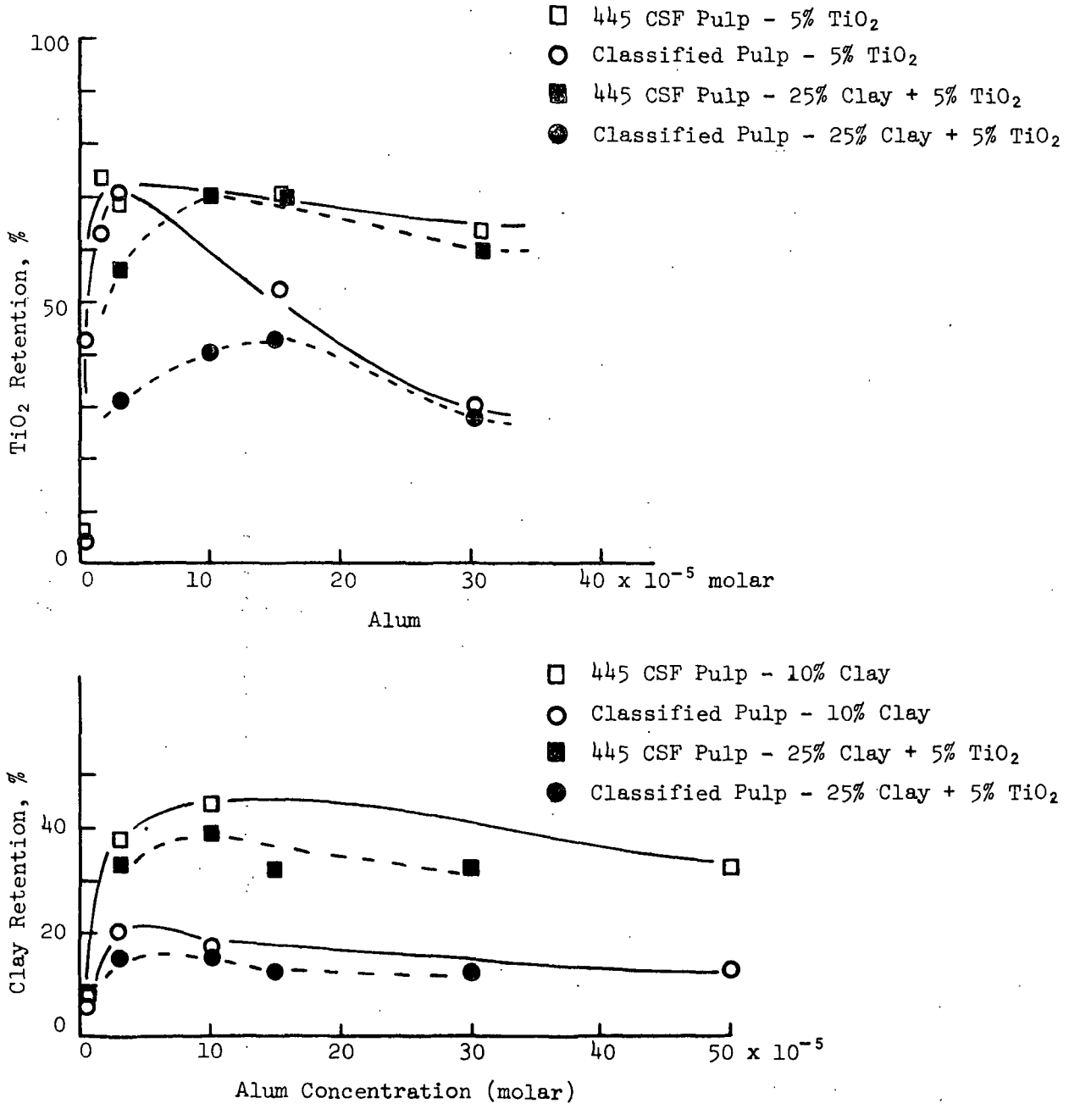


Figure 6. The Effect of Alum Concentration on Clay and TiO_2 Retention for Classified and Unclassified Pulps with Single and Mixed Pigment Systems

clay retention is quite inferior to the TiO_2 retention, some of the TiO_2 is carried out with the clay, thus effectively reducing the retention on the fiber. Such an explanation, of course, is speculative. In the case of the 445 CSF pulp, the zeta potentials of the clay and TiO_2 are not so different (Fig. 3 of PR1) weakening the above argument. On the other hand, as Fig. 6 illustrates, the effect is less in the pulp containing fines. Any explanation of the observed decrease in clay retention in the presence of the TiO_2 is more difficult at present.

The Multiple Recycle of White Water

Titanium Dioxide

Figure 7 depicts the single pass retention of TiO_2 in a recycled white water system. Unless otherwise noted, each cycle new fiber and filler were added to the furnish. "Single pass" retention here refers to the amount of material retained as a percentage of the total filler solids present in the furnish. The latter value increases in each subsequent cycle until steady state conditions are reached. This is described later. For all experiments the standard hard water with $SO_4^=$ (Table I) was used.

Figure 7 reveals that during the first few cycles a significant decrease in the single pass retention occurs. These results are similar to those noted in Table I of PR1. At the 5% TiO_2 (based on fiber) concentration (Experiment 200) the single pass retention continues to decrease only slightly after the 3rd or 4th cycle. By contrast, the results at 15% TiO_2 (Experiment 213), where filler was only added for four cycles but alum was added for eight cycles, show a very large decrease in retention after the fourth cycle (pH was maintained at 5.0). When both filler and alum were eliminated after the fourth cycle (Experiment 222), however, the single pass retention remained nearly constant, and the

zeta potential dropped to zero in the last cycles. The zeta potential result can be explained by recalling that the incoming fiber after the fourth cycle will be anionic in the absence of alum.

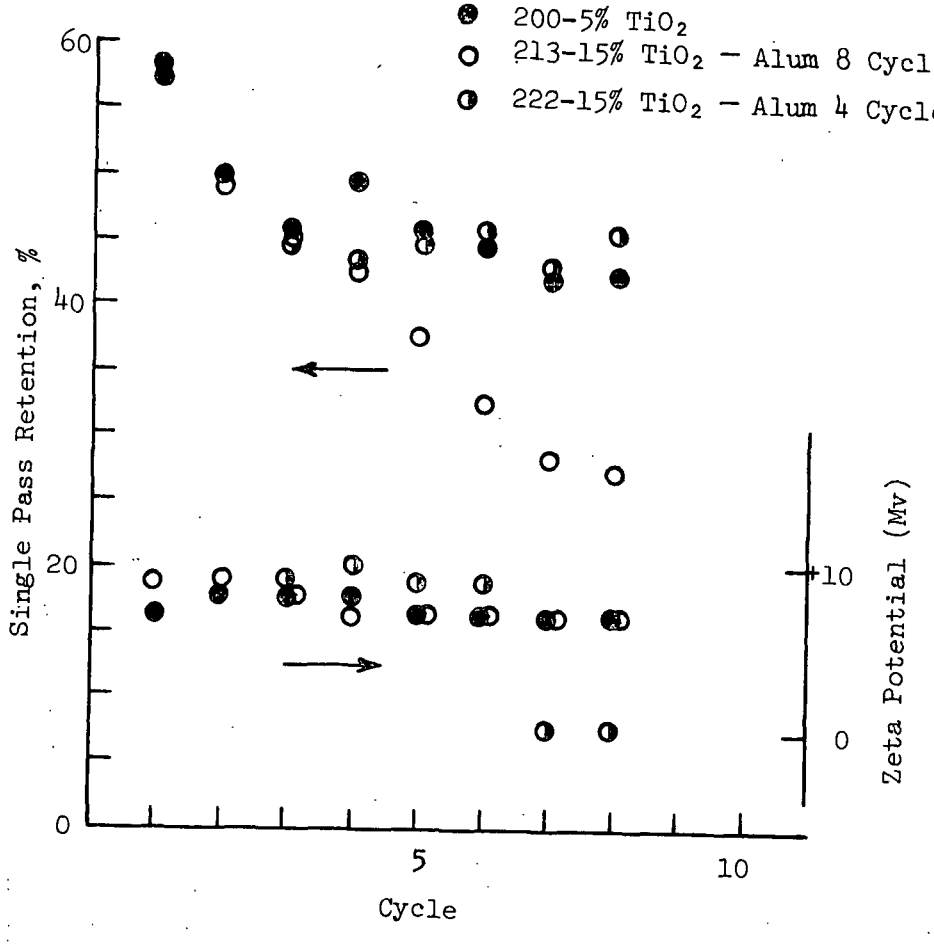


Figure 7. The Effect of Recycling on Single Pass Retention of TiO_2 and Zeta Potential of White Water Fines

In the above situation where alum and fiber only were added, it may be that the fibers become cationic. Such an effect is observed in the results of PR1 (Fig. 4) on the classified pulp. If this is the case, the increase in the cationic state resulting from the alum addition in each cycle could explain the large decrease in single pass retention of the recycled TiO_2 filler.

The recycle process described herein represents a transient phenomena in comparison to an actual papermaking system. The paper machine operates, ideally, under steady state conditions. An amount of filler added per unit time, as a percentage of the fiber added per unit time, would be expected to be carried out in the end product in the same percentage. The furnish, however, contains a larger proportion of filler to fiber, in the completely closed white water system. It is informative to estimate the degree to which the experiments described here approach steady state conditions. This can be done as follows assuming a completely closed system.

Define $\underline{R}$ as the single pass retention for each cycle. Further assume $\underline{R}$ is a fraction independent of cycle. The filler material lost to the white-water is $\underline{Z}$ (= 1-$\underline{R}$). At the start of each cycle the same amount of filler material, $\underline{X}$, is added as a percentage of dry fiber added. After $\underline{N}$ cycles it is easily shown that the filler present in the furnish is $\underline{F_N} = X\sum_{i=1}^{N} Z^{i-1}$. The percent filler retained (based on fiber) during the $\underline{N^{th}}$ cycle is

$$R_N = XR \sum_{i=1}^{N} Z^{i-1}.$$

As $\underline{N}$ becomes very large ($\underline{N} \rightarrow \infty$), the series limit becomes $(1 - \underline{Z})^{-1}$, or $\underline{R}^{-1}$. Thus, as the cycle number increases, $\underline{R_N}$ asymptotically approaches $\underline{X}$, the add-on level, i.e., $\underline{R_\infty} = \underline{X}$. This behavior is shown in Fig. 8 which depicts $\underline{R_N}$ versus cycle number for a unit add-on level $\underline{X}$. Curves corresponding to five different values of single pass retention are shown. Clearly as the single pass retention decreases, the number of cycles to achieve, say, 0.95 of the filler addition level increases significantly, with a corresponding increase in the filler content of the furnish.

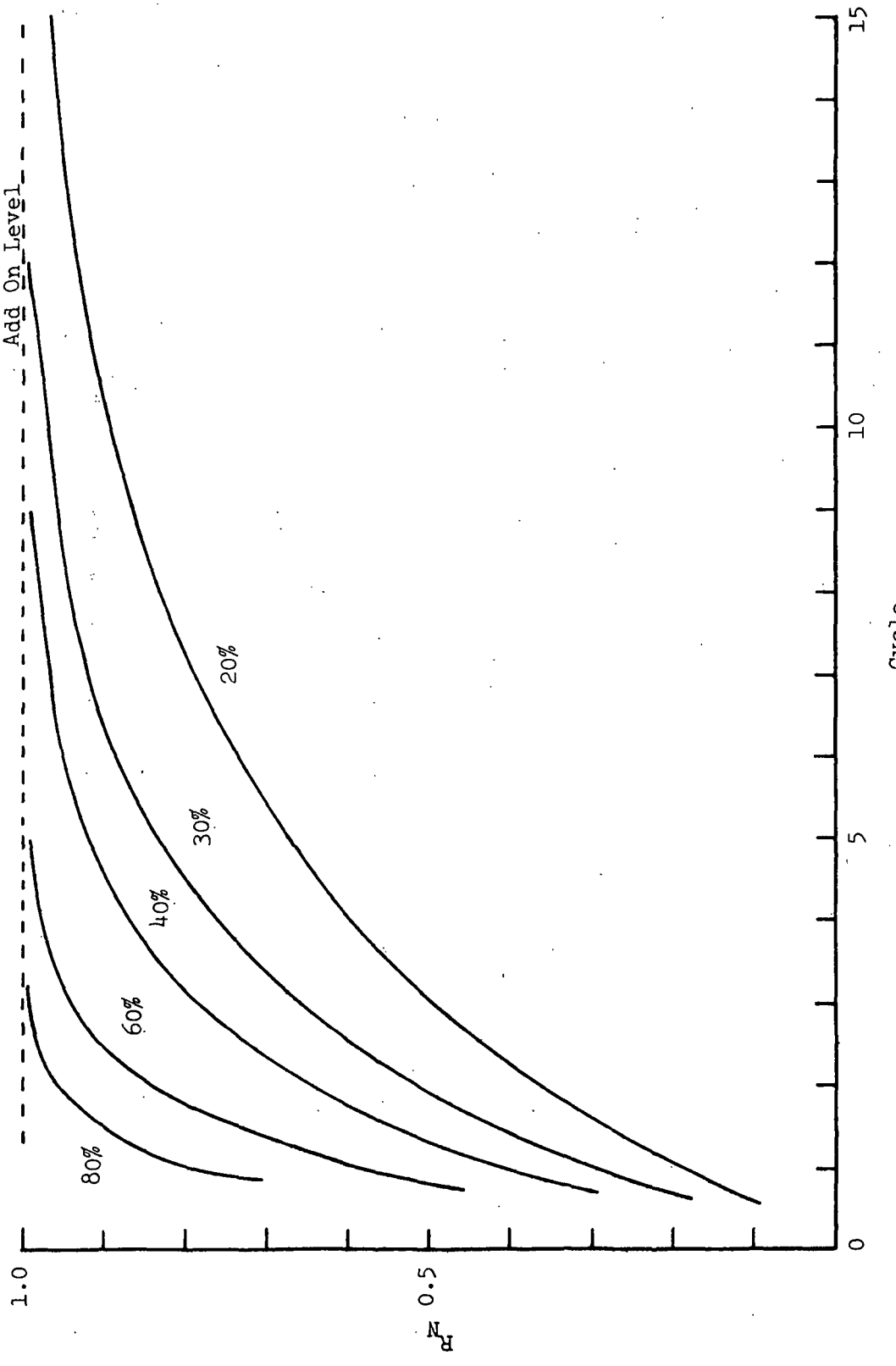


Figure 8. Theoretical Plot of Overall Retention versus Cycle Number for Various Values of Single Pass Retention

The equations for R_N and F_N, although developed for filler material retention, apply equally well to any furnish component. All that is required is a single pass retention value for the component in question, assumed independent of cycle number, and a known add-on level. Under steady state conditions (large N), the material retained per cycle and the material added per cycle are the same, and the furnish concentration of the component is F_N (N large) = $\frac{X}{R}$. In a paper-making system, when material is added via a pipe, per unit time, the above equations would be replaced by differential equations.

Sometimes it is convenient to talk in terms of the amount of material retained relative to a unit add-on level. This is referred to as a unit retention, R_u, defined as

$$R_u = (R_N/X) = R \sum_{i=1}^{N} Z^{i-1}.$$

It is interesting to note that if a single addition, Y, of a furnish component is made prior to the first cycle, and no further additions are then made, the cumulative retention after N cycles is

$$R_N^C = R \sum_{i=1}^{N} Z^{i-1}.$$

This equation describes a single addition, but a cumulative retention, and is the same expression found for the unit retention, R_u, when material is added each cycle. This latter fact can be understood with only a little thought.

Figure 9 shows the measured retention values versus cycle. Also shown are the theoretical retention values, R_N. If the single pass retention is independent of cycle, that is, independent of increasing filler and fines levels and ion buildup in the furnish, then the measured values should be consistent

with the theoretical values. The theoretical curves were calculated using the mean of the single pass retention values shown in Fig. 7. The tendency of the data points to fall beneath the calculated curves results from the decreasing single pass retention as shown in Fig. 7. Figure 9 shows that about 90% of the steady state value has been achieved after 4 cycles.

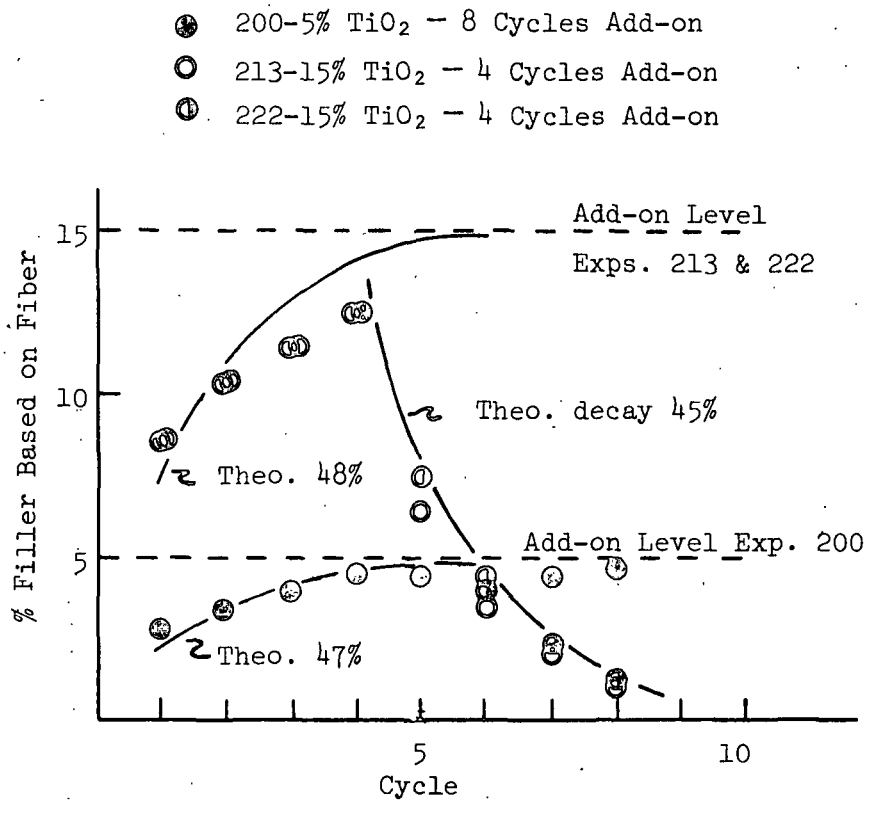


Figure 9. Comparison of Theoretical Retention Curves with Measured Retention in a Recycle System

Optical Results

The specific scattering coefficients at the two wavelengths 457 and 572, are shown in Fig. 10a and 10b, respectively, plotted against the percent TiO_2 in the sheet. Clearly the points do not fall on a single straight line. The numbers by the data points correspond to the cycle number.

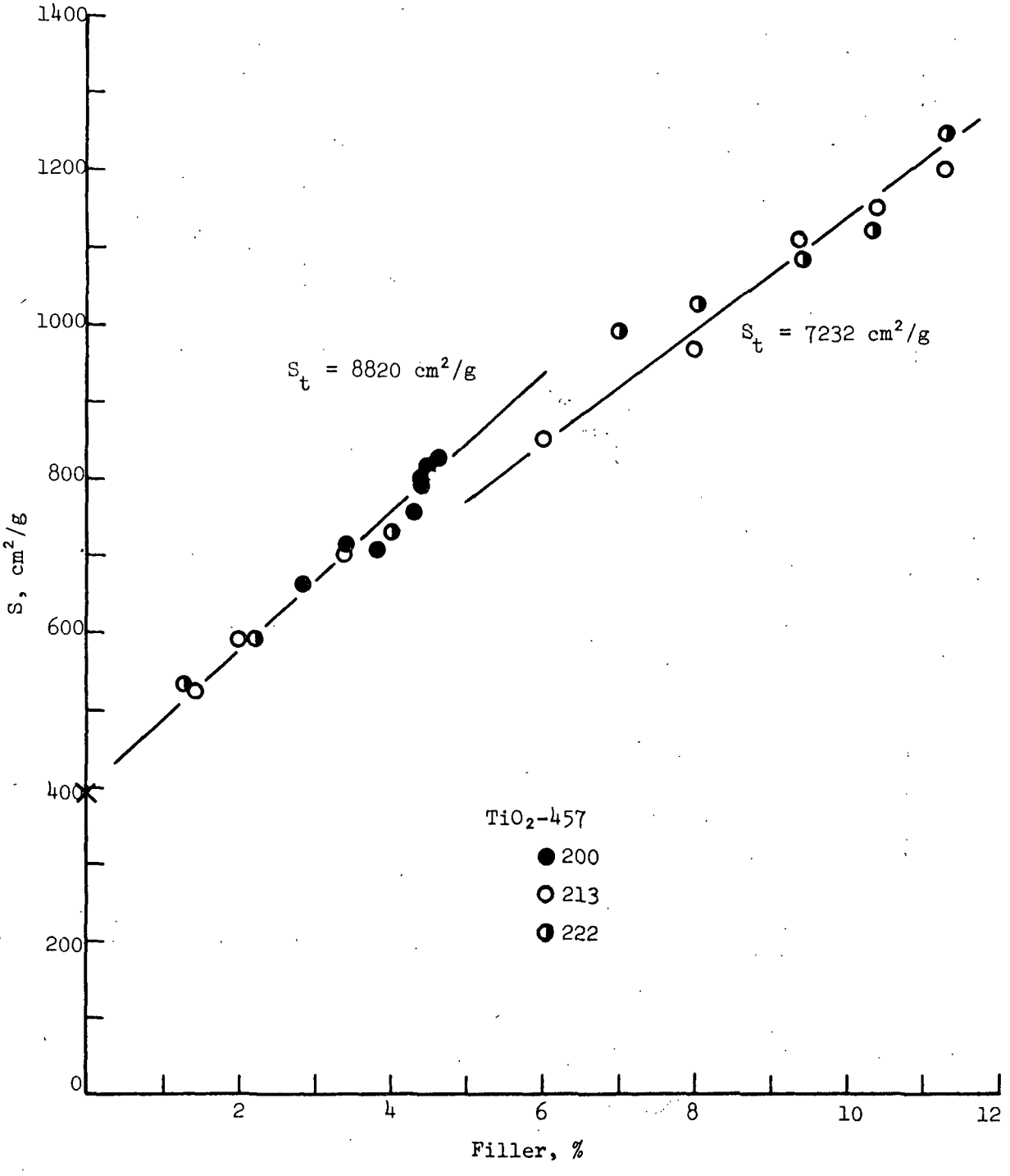


Figure 10a. Scattering Coefficient versus % TiO_2 in the Sheet Measured at 457 μm

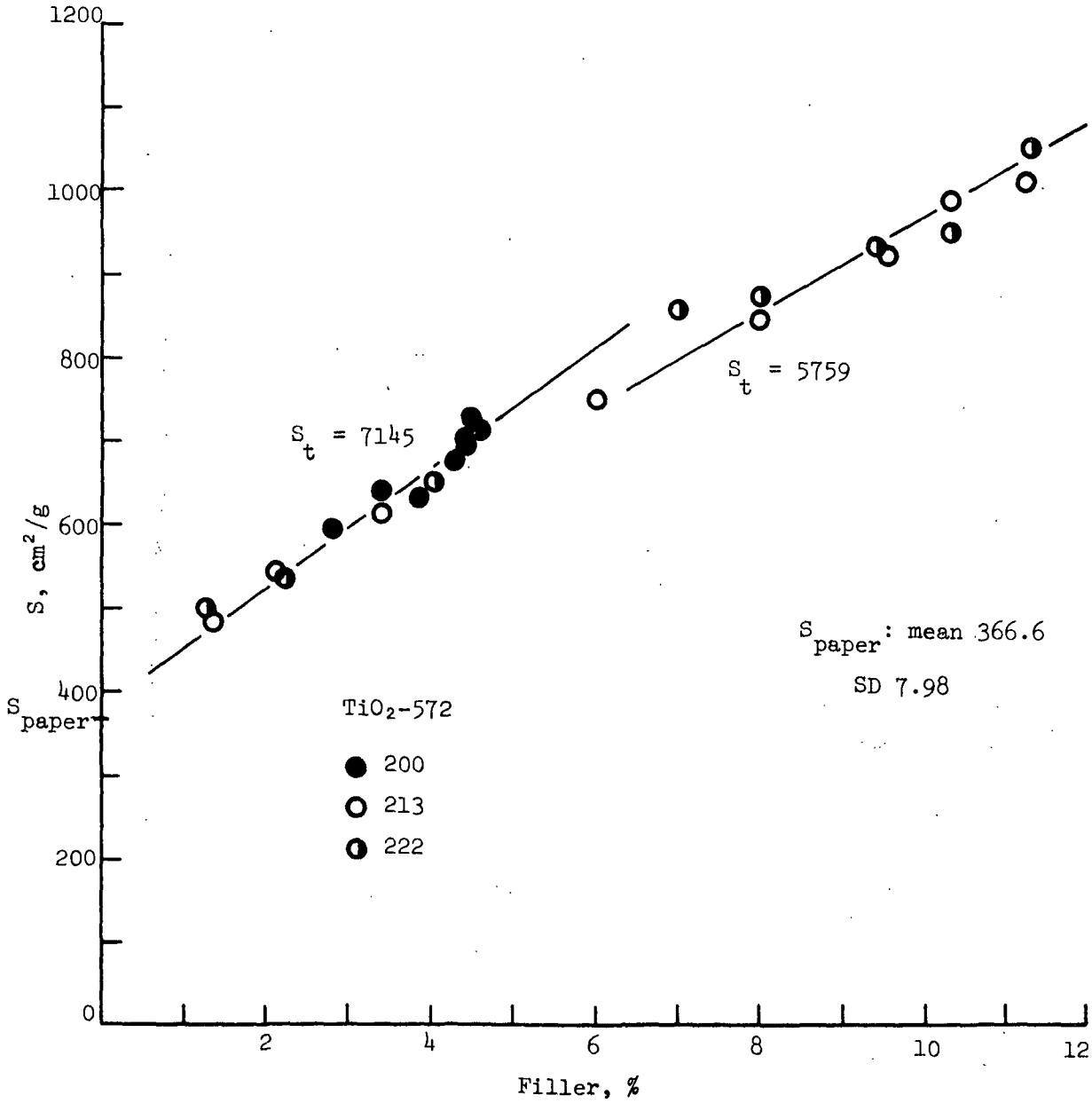


Figure 10b. Scattering Coefficient versus % TiO_2 in the Sheet Measured at 572 μm

The straight lines shown on these figures are least squares linear regression lines. These have been fitted to the high and low loading regions of the paper and include the specific scattering coefficients of the paper only, S_1, as indicated on the ordinate axis. In general the $\underline{S}_t$ values deduced from slopes of these curves are less than those found in PR1, a consequence of the effect of the hard water in the present system.

These data, however, are similar to those reported in PR1, in that they show the same nonlinear behavior with percent filler in the sheet. These multi-cycle results reinforce the earlier conclusion that recycled pigment is redispersed and upon subsequent retention displays an optical benefit comparable to that material retained on the initial cycle. For example, that material which is retained in the latter cycles of Experiment 200 is apparently quite as good optically as that retained in the earlier cycles, as all the points fall near the least squares linear regression line with $S_2 = 7145$ cm^2 gm^{-1}. In addition, those points of Experiments 213 and 222 obtained from cycles 5 through 8, where no additional TiO_2 was added, also fall along this same line. Once again this suggests the possibility that any recycled pigment, subsequently retained, has been redispersed to such an extent that it behaves, optically, similar to material retained on the first pass at the lowest loadings.

In an attempt to expand on the above discussion, the pigment specific scattering coefficient, $\underline{S}_t$, was computed from $\underline{S} = \underline{S}_p + (\underline{S}_t - \underline{S}_p)\,\underline{f}_t$. These values are shown in Fig. 11 for the highest loadings *versus* cycle number. During the first 4 cycles, with fiber and 15% TiO_2 being added each cycle, virtually no change in $\underline{S}_t$ is observed with cycle number. However, during cycles 5-8, with no additional TiO_2 added, the value of $\underline{S}_t$ increases. The value of $\underline{S}_t$ then seems to be related to the loading in the furnish, increasing as the loading decreases.

If there has been agglomeration of filler material in the white water which would tend to increase particle size and hence decrease S_t, that material must not remain in the agglomerated state upon retention in a subsequent cycle. If it did, the value of S_t beyond 4 cycles in Fig. 11 would be expected to decrease, not increase. At the lower loadings (5% add-on), S_t was essentially independent of cycle.

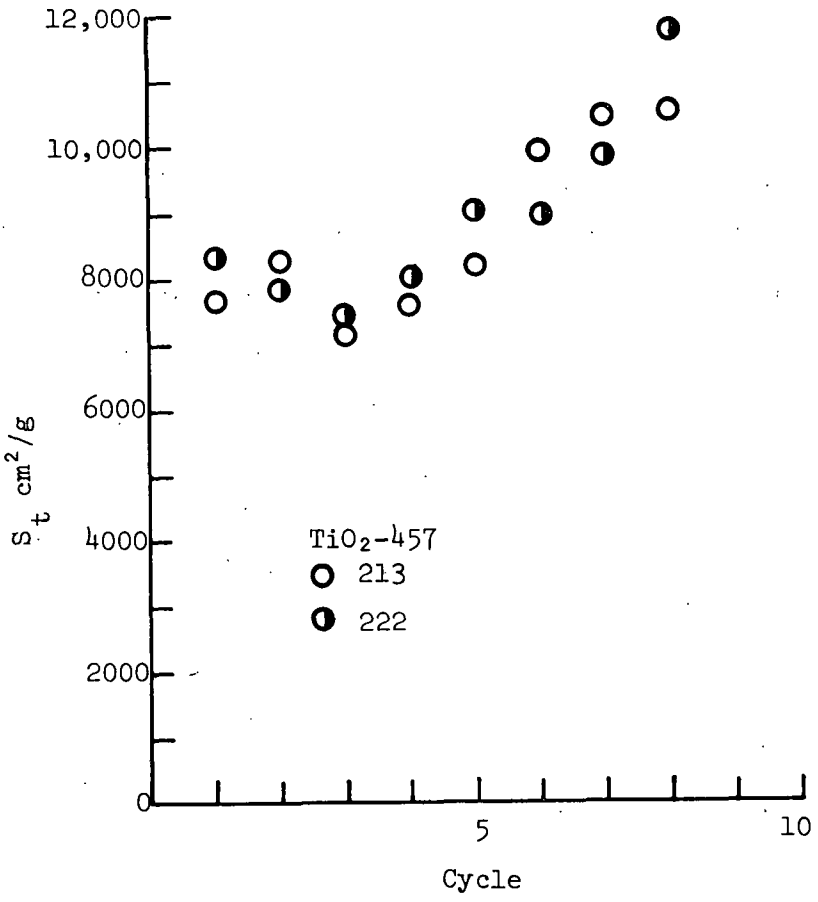


Figure 11. TiO_2 Pigment Specific Scattering Coefficient *versus* Handsheet Cycle Number

The effect of the loading in the furnish (percent TiO_2 based on fiber) on the value of S_t is shown in Fig. 12. Here we see direct evidence that self flocculation must be occurring. Although there is a fair amount of scatter in the data there can be little question that S_t decreases with percent TiO_2 in the furnish. This effect has been observed before (4). The effectiveness of

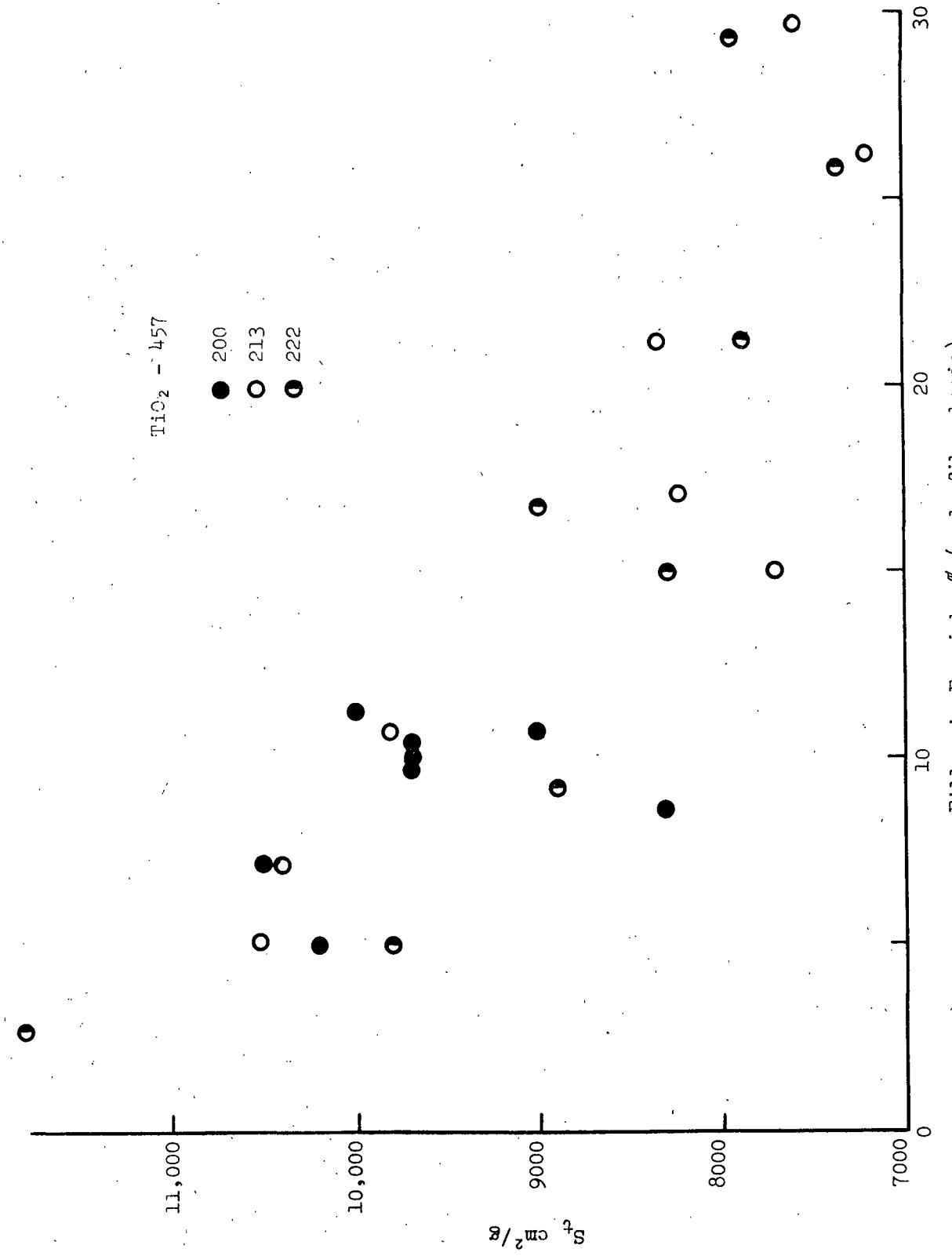


Figure 12. TiO_2 Pigment Specific Scattering Coefficient versus % Filler in the Furnish

the material in providing a desired optical benefit is directly related to the furnish filler content. This interesting result takes on additional significance if we also examine the single pass retention of TiO_2 *versus* the percent filler loading in the furnish as depicted in Fig. 13. Here we see that, for the conditions examined, there is no dependence of retention on loading.

The last three figures suggest that in the multicycle system examined there is no detrimental effect on retention or the value of S_t due to the recycle of material. The latter figures, however, indicate that high retentions in a system with high loadings of filler in the furnish may not give a correspondingly high value for S_t. Rather, Fig. 12 illustrates that the optimum pigment specific scattering coefficients for TiO_2 will occur only at the lower loadings.

As we will soon see, the same arguments do not apply to clay fillers.

The specific absorption coefficients for the TiO_2-containing handsheets have values comparable or slightly less than the pulp only handsheet.

CLAY

Retention Results

The single pass retention values *versus* cycle for the clay studies are shown in Fig. 14. There is only a slight decrease in retention at the higher cycles. Figure 15 gives the percent of clay filler retained in the handsheet *versus* cycle. As before, we observe that the data tends to fall slightly beneath the theoretical curves. The theoretical curves were computed, as noted earlier, using the mean of the single pass retention values obtained at the two loading levels.

As observed in the TiO_2 results, the departure of the data from the theoretical curves is greatest at the higher loadings.

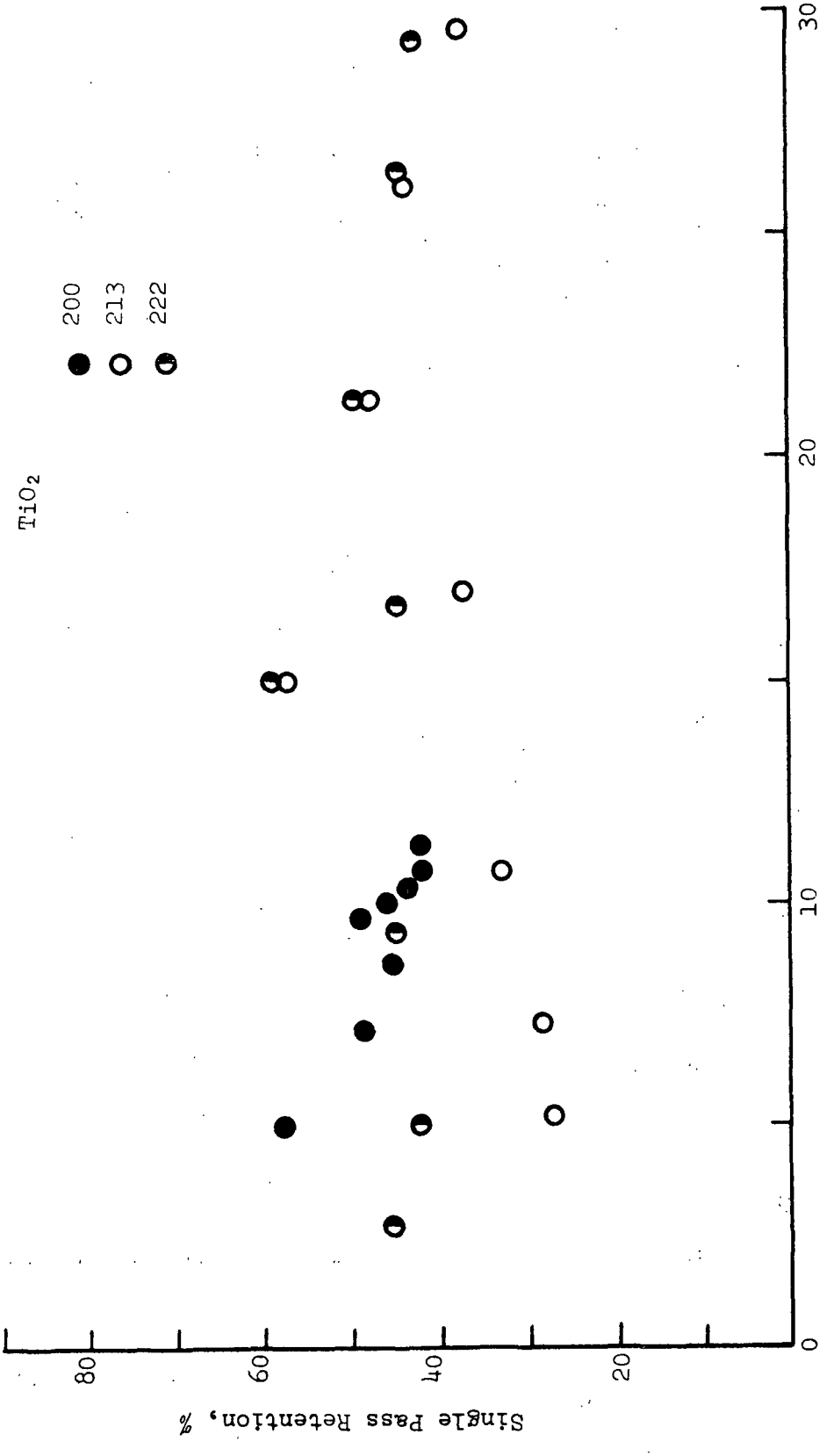


Figure 13. Single Pass Retention of TiO_2 versus % Filler in the Furnish

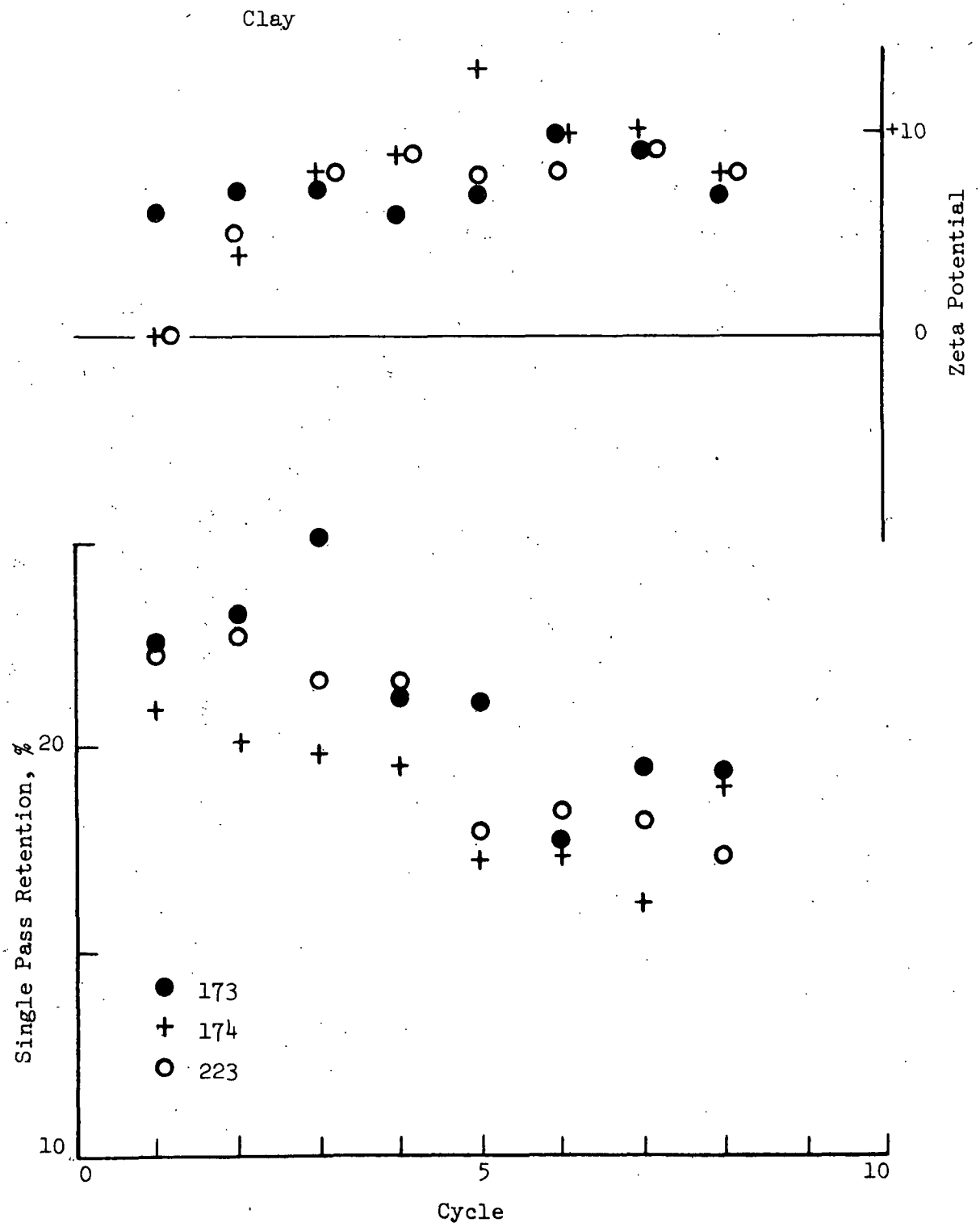


Figure 14. A Comparison of Zeta Potential and Single Pass Retention of Clay versus Handsheet Cycle Number

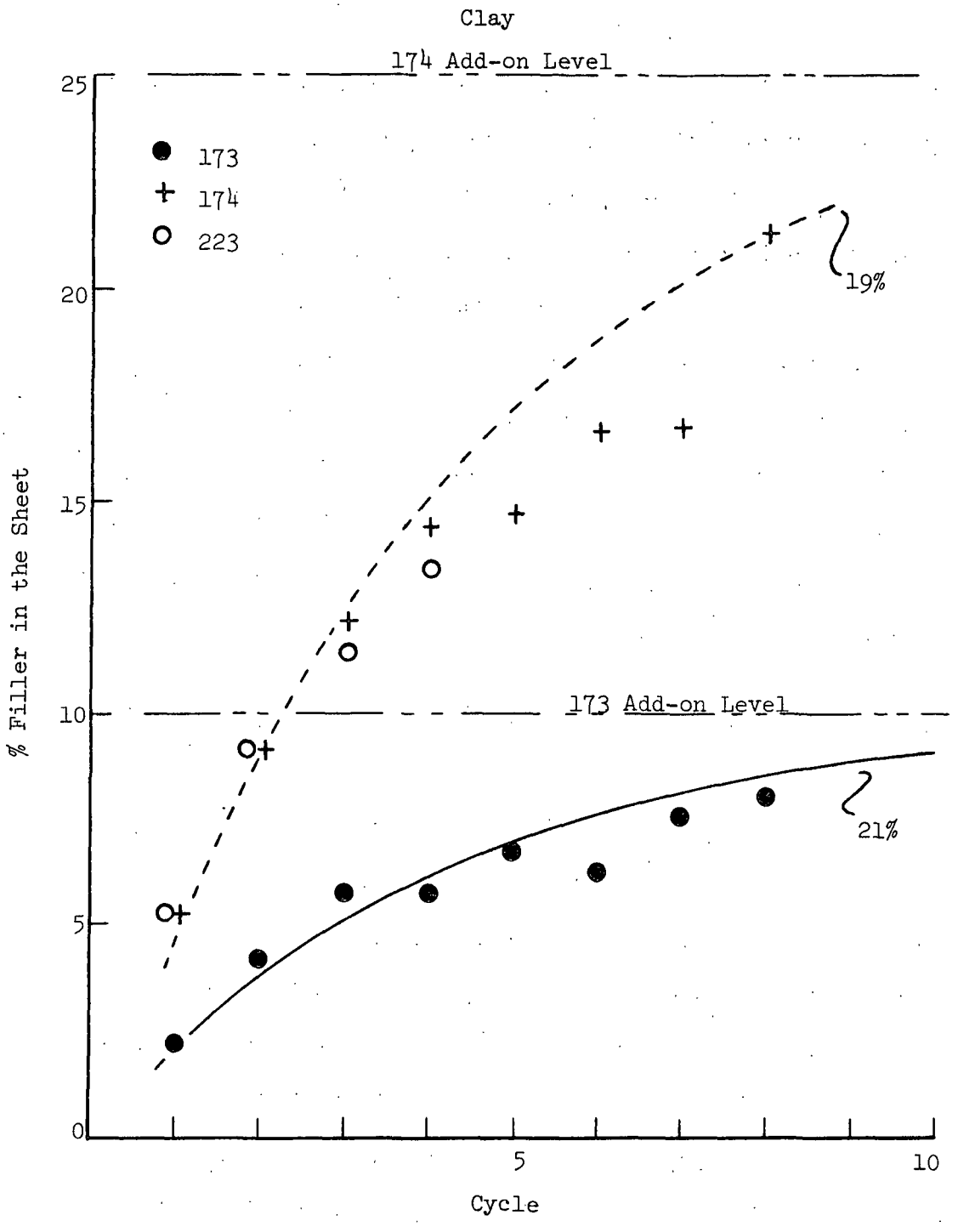


Figure 15. % Filler in the Sheet versus Handsheet Cycle Number

Optical Results

Figures 16a and 16b give the specific scattering coefficient for the clay studies versus percent clay filler in the sheet. The results are similar to those obtained in Phase I at lower loadings. The present results, however, are extended to much higher loadings and the value of S does depart from linearity beyond about 10% clay in the sheet. As noted in the TiO_2 work, there does not seem to be any dependence of S on cycle. Those cycles of Experiment 223, for example, during which no additional clay was added to the system, still fall near the main curve. The value of S_c for the pigment was calculated and shown versus cycle in Fig. 17. There appears to be a slight decrease in S_c with cycle according to the linear regression line shown, but the scatter of the data makes this latter interpretation debatable.

In contrast to the TiO_2 results, S_c is not significantly affected by the clay loading in the furnish, as shown in Fig. 18, whereas the single pass retention, Fig. 19, does appear to be dependent upon loading. The single pass retention decreases about 25% over the range of loadings shown in Fig. 19. These clay results indicate that high furnish loadings lower the single pass retention but do not seem to affect the pigment scattering coefficient, S_c. Recycled pigment, when retained, has an S_2 value comparable to material retained on the first pass. For example, cycles 1 and 8 of Experiment 223 illustrate this (Fig. 18). Point 8, corresponding to the 8th cycle, was material that had been recycled at least five times, since no clay had been added after the 4th cycle. It compares favorably with material retained on the first cycle, point 1. Thus any clay agglomerated in the white water must have been restabilized before being retained.

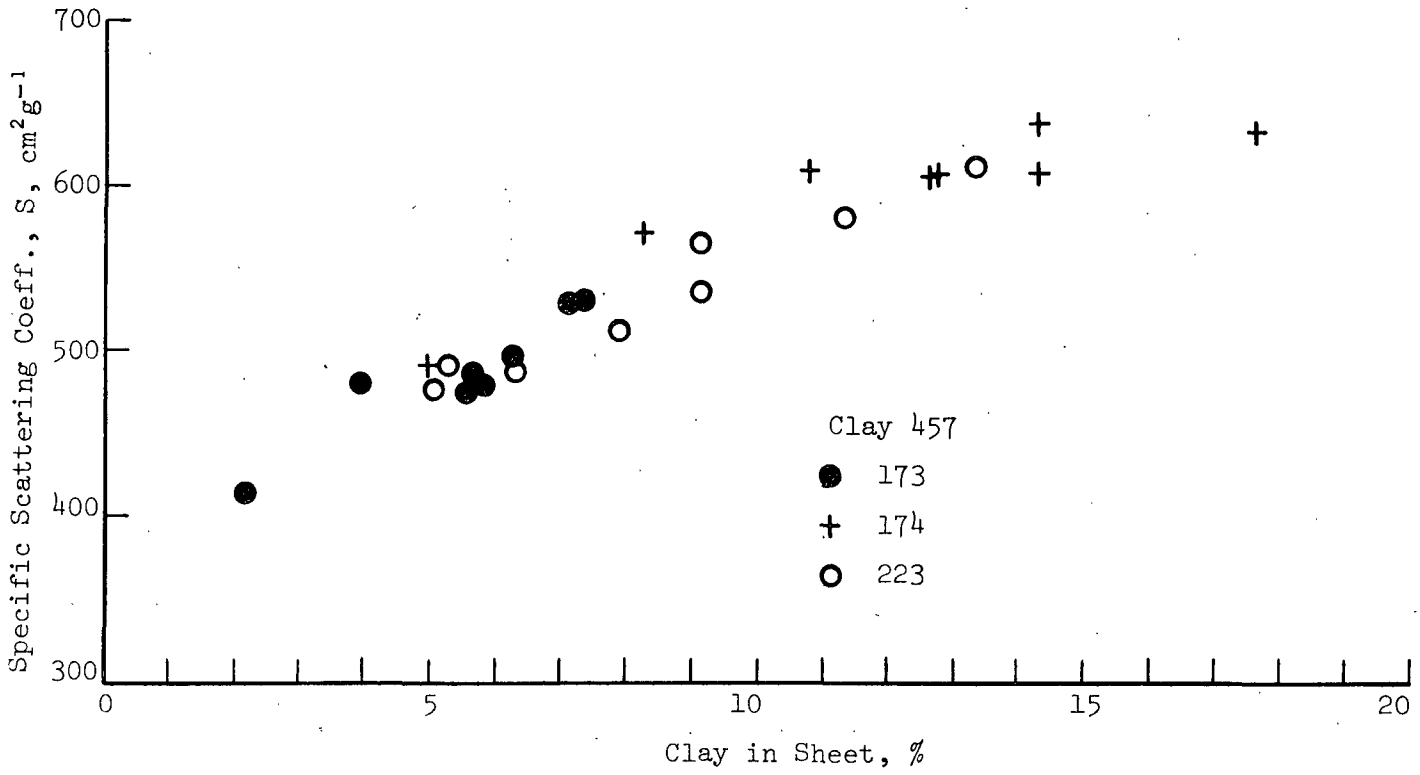


Figure 16a. Specific Scattering Coefficient versus % Clay in Sheet Measured at 457 µm

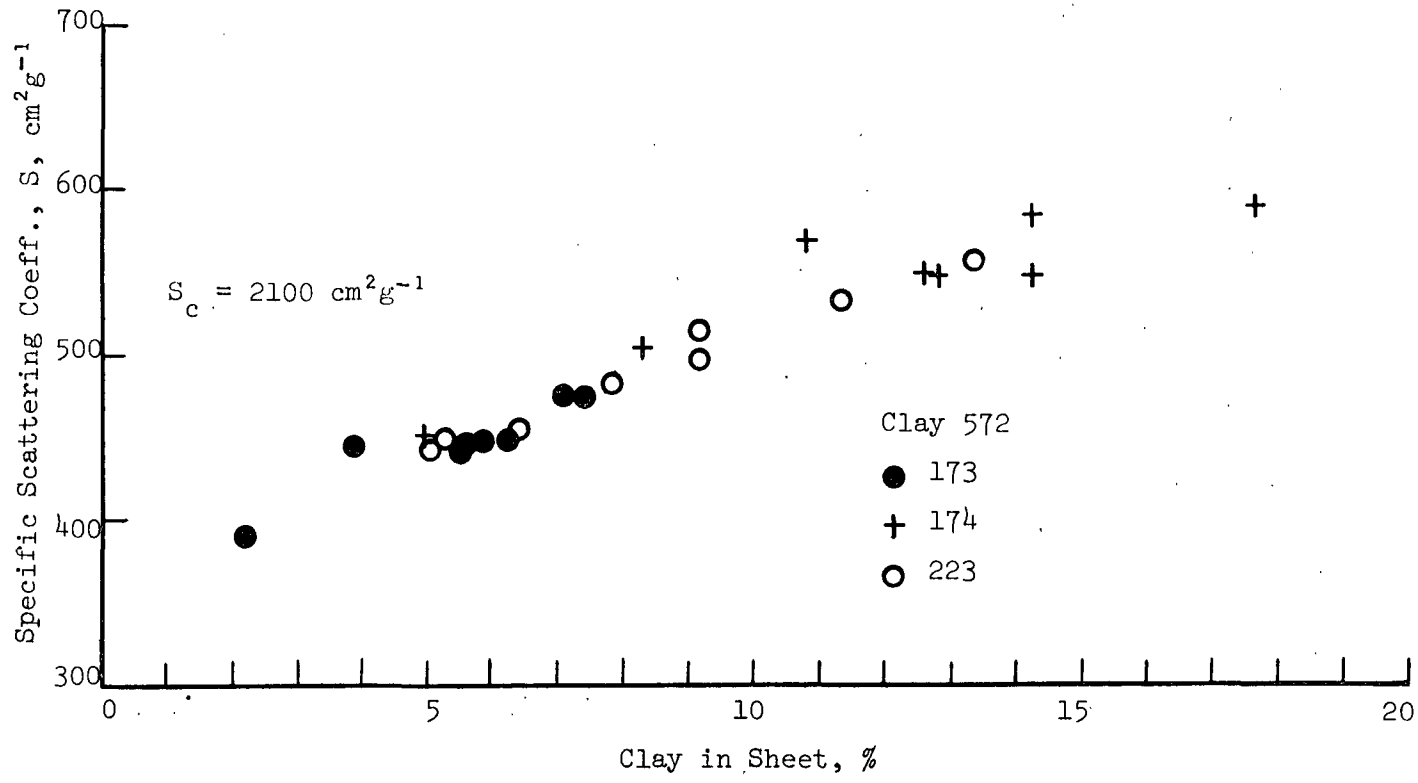


Figure 16b. Specific Scattering Coefficient versus % Clay in Sheet Measured at 572 µm

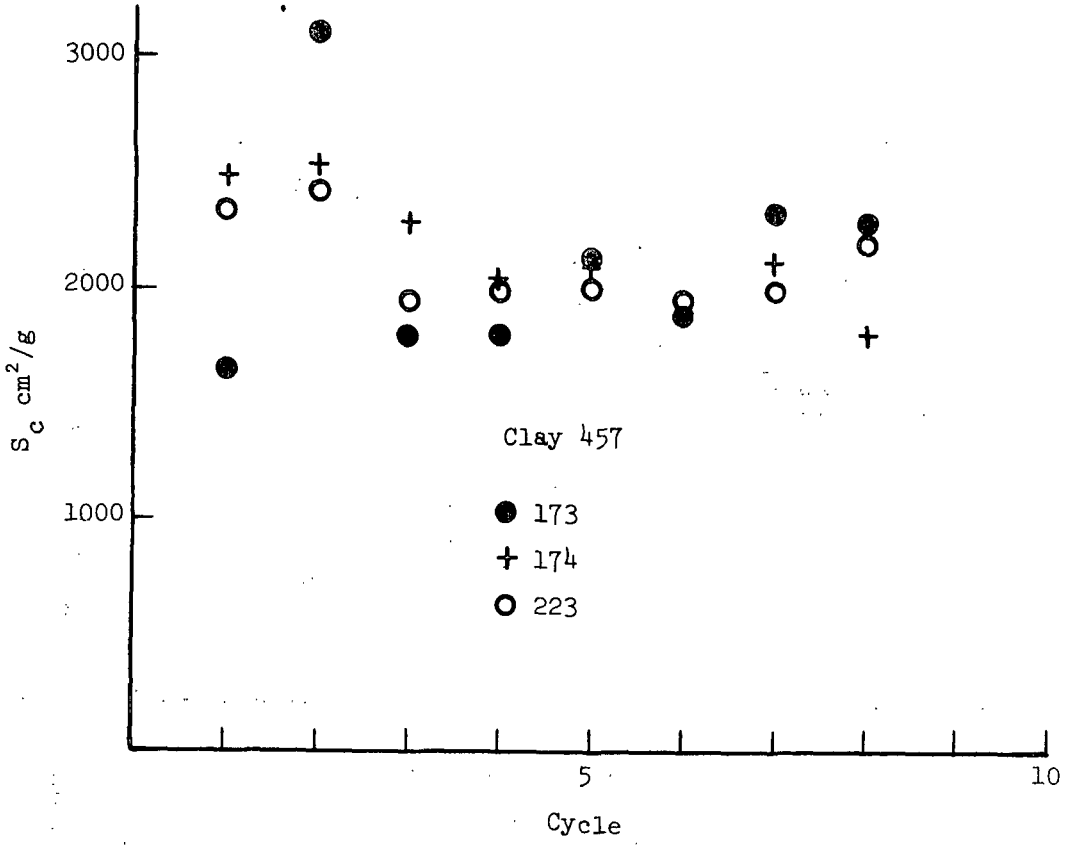


Figure 17. Clay Pigment Specific Scattering Coefficient versus Handsheet Cycle Number

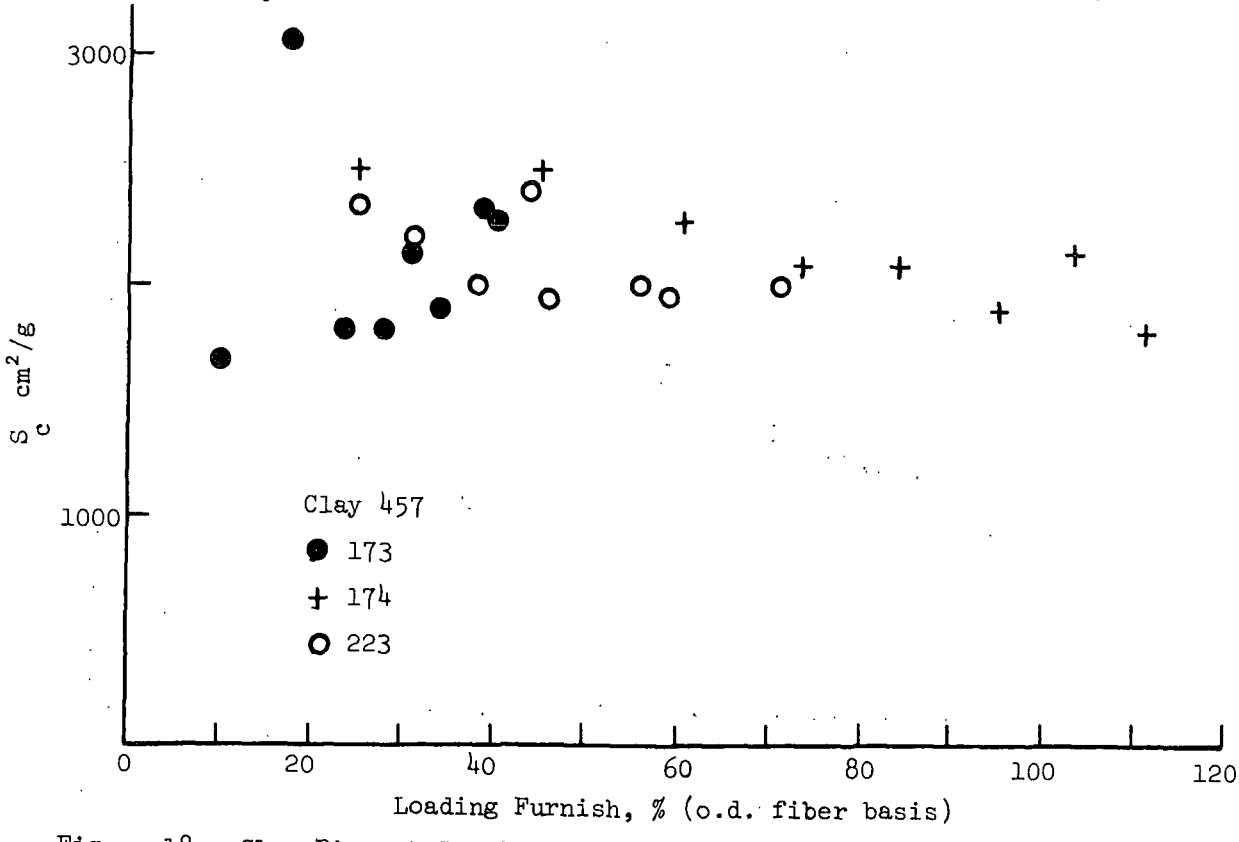


Figure 18. Clay Pigment Specific Scattering Coefficient versus % Filler in Furnish

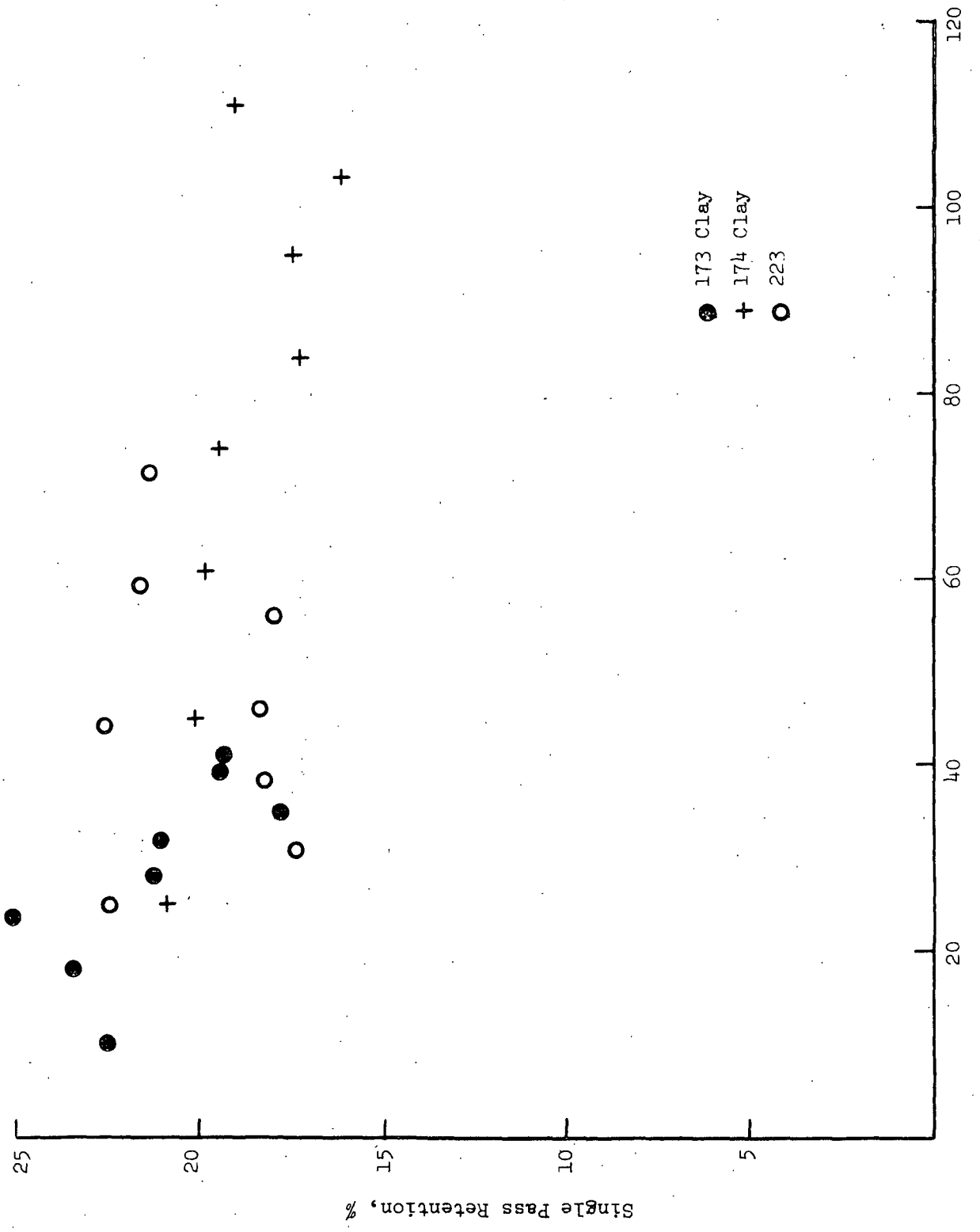


Figure 19. Single Pass Clay Retention versus % Filler in Furnish

The specific absorption coefficients versus percent clay in the sheet are presented in Fig. 20a and 20b for the two wavelengths. The results are similar to those reported in PR1, except in this case higher filler levels in the sheet are obtained.

Fines Loss and White Water Ion Concentrations

The fines lost to the white water in the multicycle systems are given in Table IV. In general there appear to be no unanticipated trends. With the exception of the clay results at high loadings, there is no apparent buildup of fines in the white water. The fines are carried out in the sheet at the same level at which they are being added. The fines loss in the pulp and TiO_2 + pulp systems are comparable. The clay plus pulp system does show an increase in fines loss over the other systems, especially at the 25% add-on level (Experiment 174). Furthermore more fines are lost as the loading in the furnish increases (as cycle number increases). Since the association of pulp fines and clay is well established, e.g., PR1, this result is not surprising. As the furnish loading is increased there is simply more opportunity for more fines to be agglomerated with clay particles which subsequently end up in the white water. The exceptionally high values for cycles 3 and 4 of Experiment 174 cannot be explained. After each cycle a sample of white water was taken and filtered. The supernatant was analyzed for changes in ion concentration during each cycle. Specific ions included Al, Mg, Ca, Cl, Na, and SO_4. In general there was a considerable amount of scatter in the data making interpretation difficult. Figure 21 depicts the results for the sulfate content. Results are shown for the pulp only, pulp plus 25% clay, and pulp plus 5% TiO_2 systems. In each case 10×10^{-5} molar alum was added each cycle. The dotted line depicts the change in concentration anticipated in the results of the pulp-only assuming no sulfate comes in with the pulp. (The Phase I results actually demonstrated that this

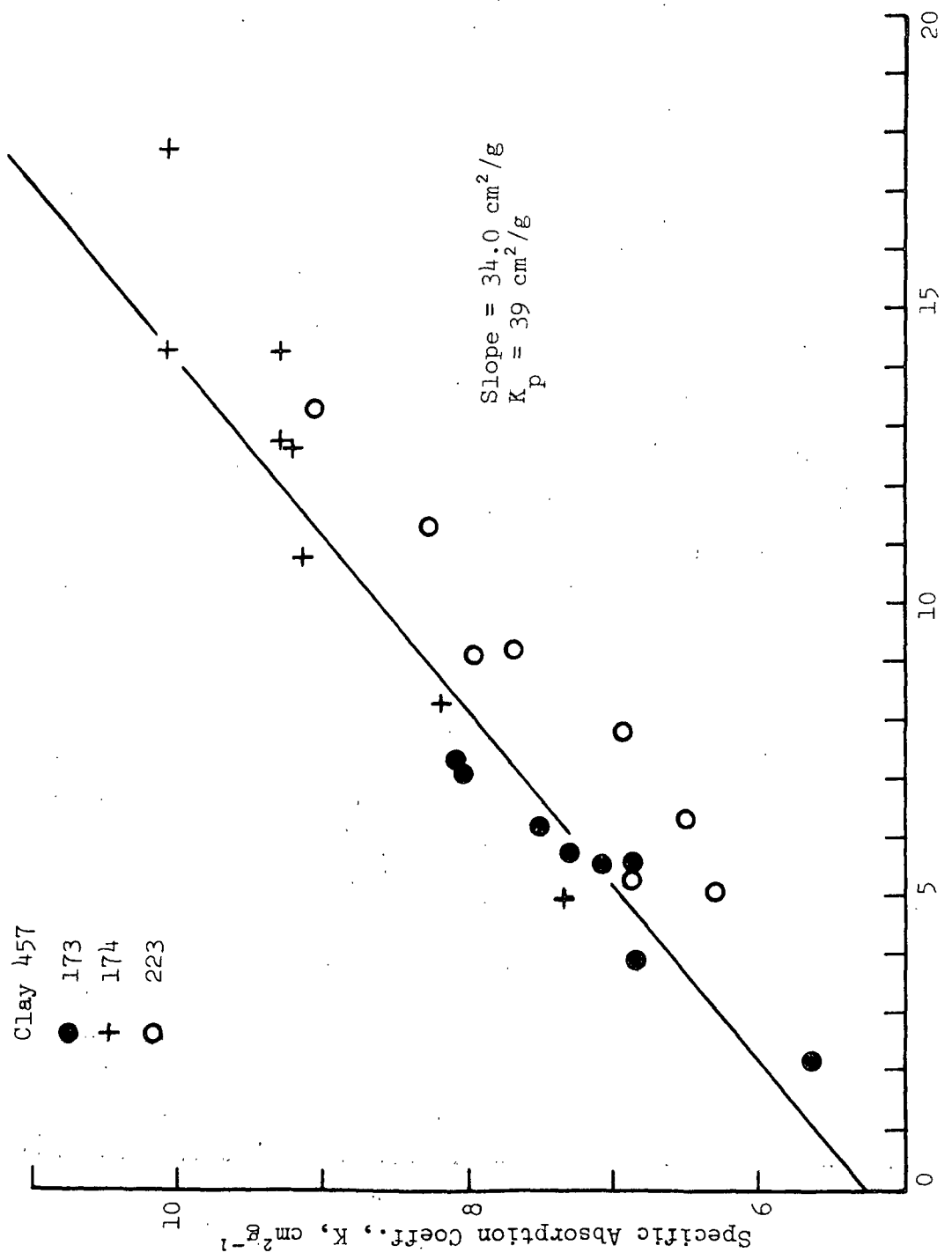


Figure 20a. Specific Absorption Coefficient versus % Clay in the Sheet Measured at 457 µm

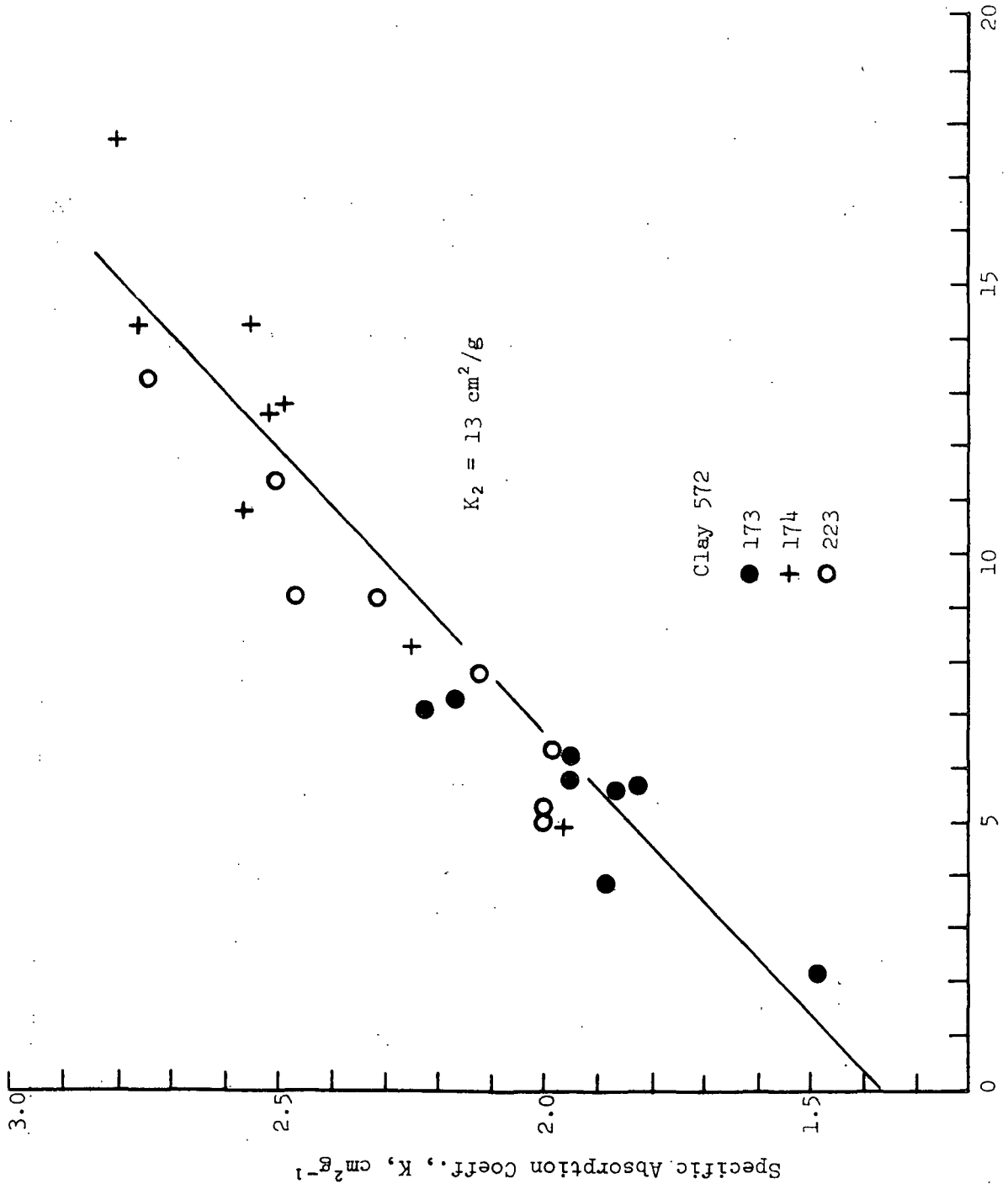


Figure 20b. Specific Absorption Coefficient versus % Clay in the Sheet Measured at 572 µm

445 CSF pulp at 0.3% consistency contributes less than 2 ppm sulfate.) The linear regression line (solid black) for this system is in fair agreement with the expected behavior. The TiO_2 results would imply that much of the SO_4^{-2} added is being retained in the sheet. The sulfate concentrations in the clay system are higher than in the pulp only system. This suggests that sulfate is coming into the systems with the clay, not an impossibility. This conclusion is not supported by the results reported in PR1 (Table XVII), however, where there is no evidence of sulfate being present in the clay.

TABLE IV

PULP FINES LOST IN MULTICYCLE EXPERIMENTS, %

(Hard water, 0.3% consistency, 2.2% alum, 70 cpm in 445 CSF pulp)

Cycle	Pulp Only	Pulp + Clay		Pulp + TiO_2	
	Expt. 171	173 (10%)	174 (25%)	200 (5%)	213 (15%)
1	2.4	2.7	2.5	1.9	2.1
2	2.0	2.5	3.1	2.4	2.0
3	2.9	3.1	4.7	2.0	2.7
4	3.3	3.3	6.0	2.9	2.5
5	2.9	2.9	3.3	2.8	2.4
6	2.8	3.2	3.7	2.6	2.8
7	2.7	2.9	4.1	3.2	3.1
8	2.6	2.8	3.8	2.9	2.7
9	3.2				
10	2.2				

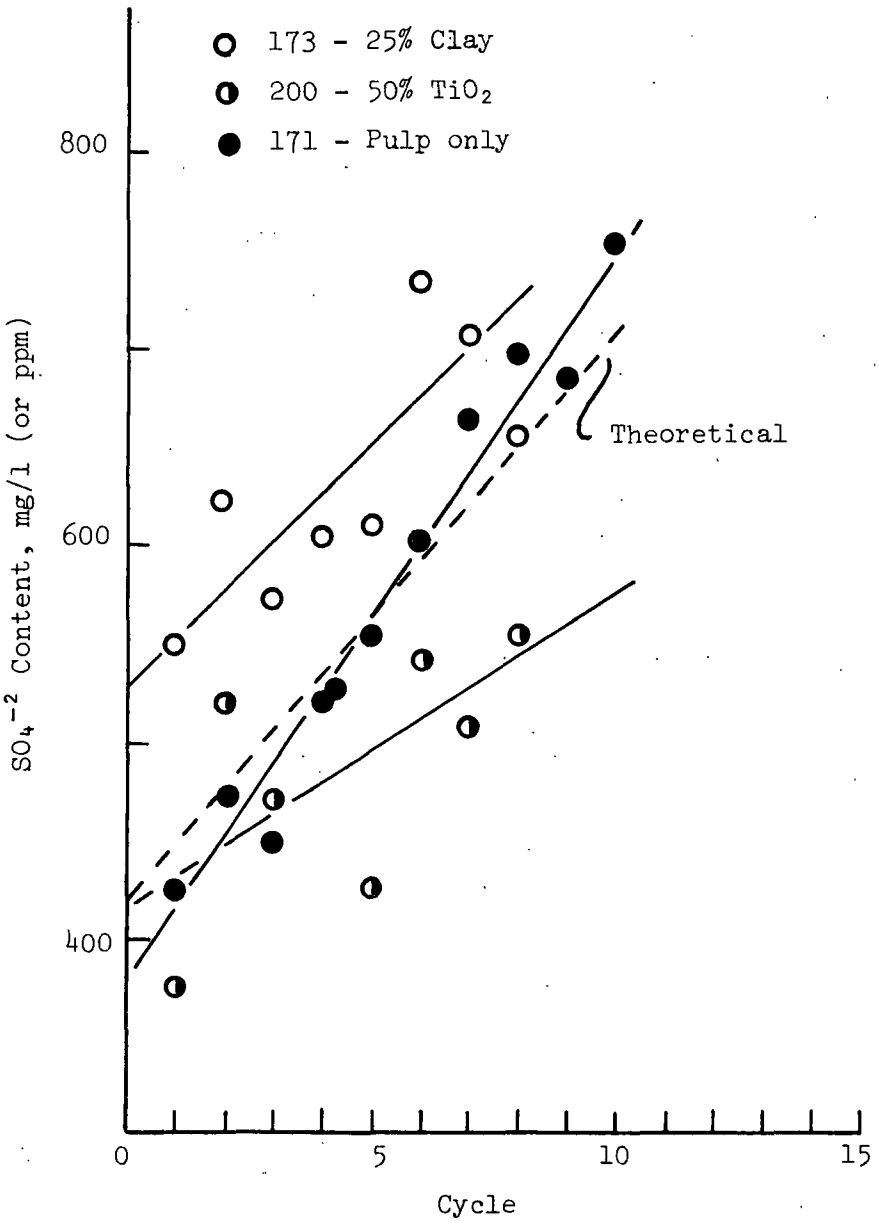


Figure 21. Concentration of Sulfate Ion in the White Water versus Handsheet Cycle Number

PART II: NEW PULP SYSTEMS

In Phase I of this program the role of fines on retention was examined using two bleached kraft softwood pulps, one classified and one with a Canadian Standard Freeness of 445 ml. This section reports on results obtained on four new systems, a classified and unclassified bleached kraft hardwood, and a classified and unclassified spruce groundwood. The specific details concerning these pulps, as well as a description of the classification procedure, are included in the experimental section. As noted earlier, the purpose in including these new pulp systems in the investigation is to further enhance our understanding of the role of pulp fines in the retention of particulate matter.

All experiments are similar to those described in PR1. In all cases the furnish was prepared with distilled water, pH adjusted to 5.0, the consistency was 0.3%, and the agitation was 70 cpm. Filler loading levels used were 5% TiO_2 and 10% clay. No clay retention studies were performed in the classified kraft hardwood (KHW-CL) system or the classified groundwood (GW-CL) pulp. No recycle experiments were performed.

RETENTION

The effect of alum concentration on the retention of TiO_2 is shown in Fig. 22 for the four new pulps. The abbreviations KHW and GW refer to kraft hardwood and groundwood, respectively. Included for comparison are the results from PR1 (Fig. 1) for the 445 CSF pulp. There is no maximum observed with increasing alum concentration. As expected, the retention in the classified systems is considerably less than the unclassified pulps pointing out once more the importance of the fines in the retention process.

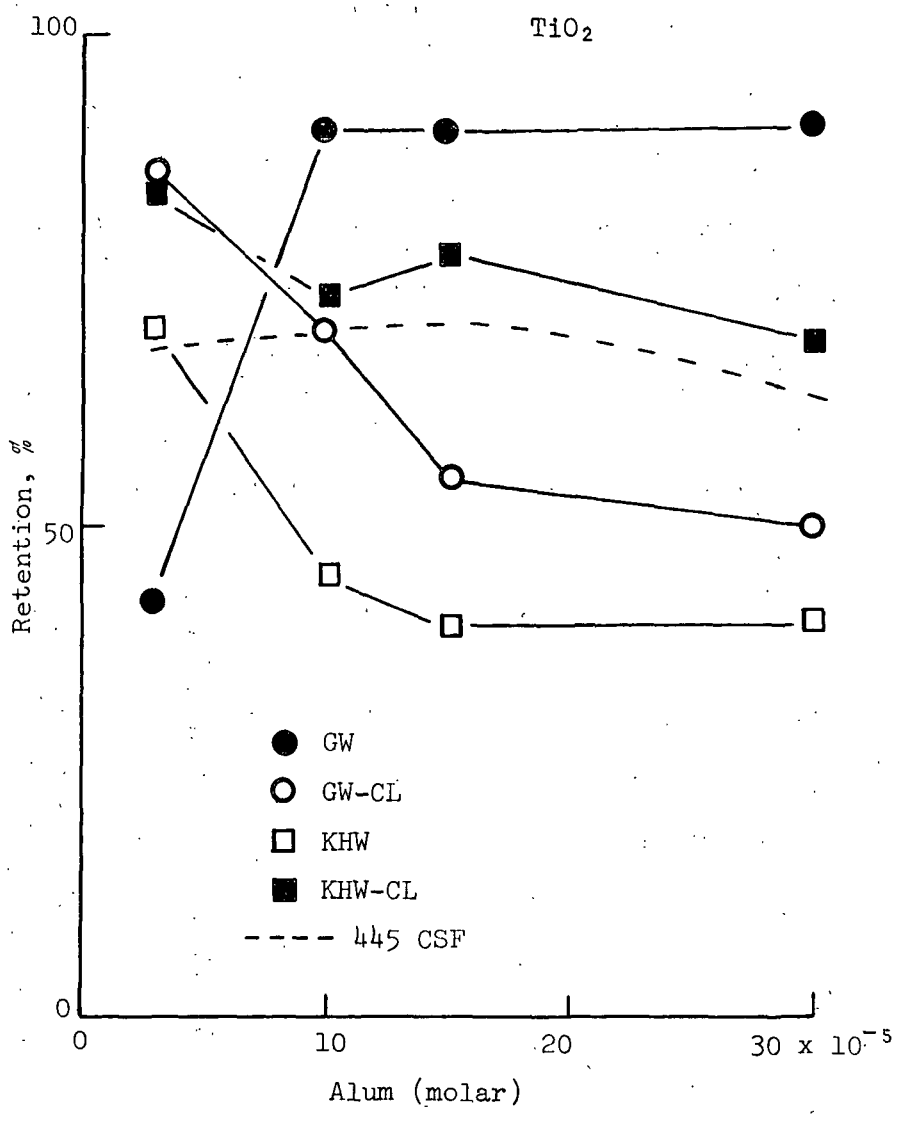
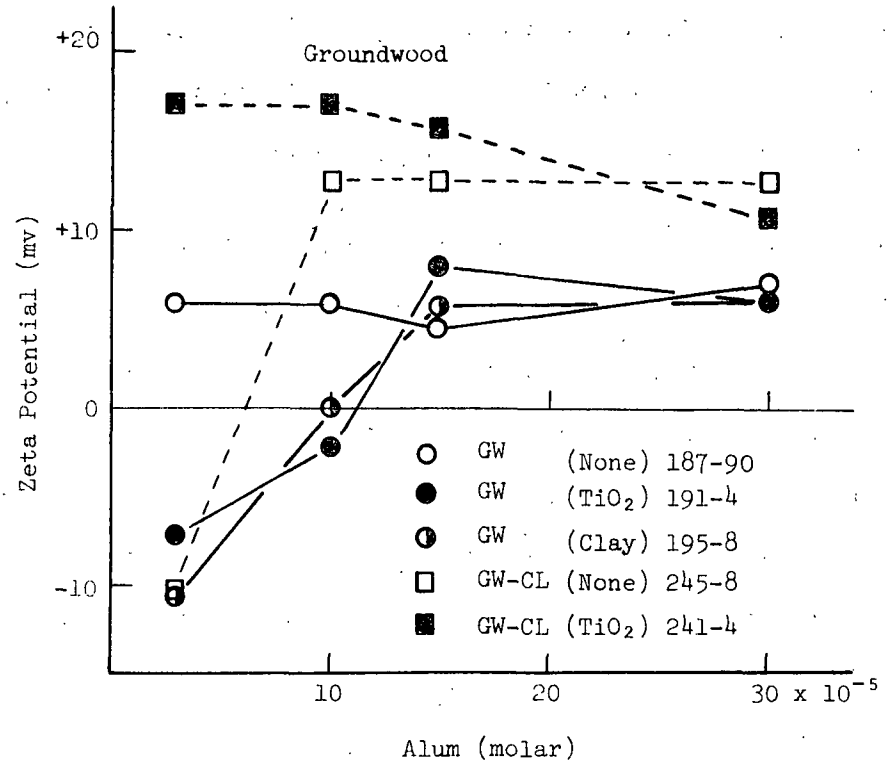


Figure 22. The Effect of Alum Concentration on Single Pass Retention of TiO_2 for the New Pulps

The zeta potential results, Fig. 23, reveal that the zeta potential for the GW and HW pulps is positive over the range of alum additions used with no filler present (open circles). In the classified systems, KHW-CL and GW-CL, open squares, the zeta potential is still negative at the lowest alum levels and becomes positive and constant by about 10 x 10^{-5} molar. A similar result is observed when TiO_2 is present in the GW or KHW systems (solid circles). This behavior, as suggested earlier, implies that the alum cations are absorbed preferentially by the TiO_2 pigment and it is the zeta potential of the fines



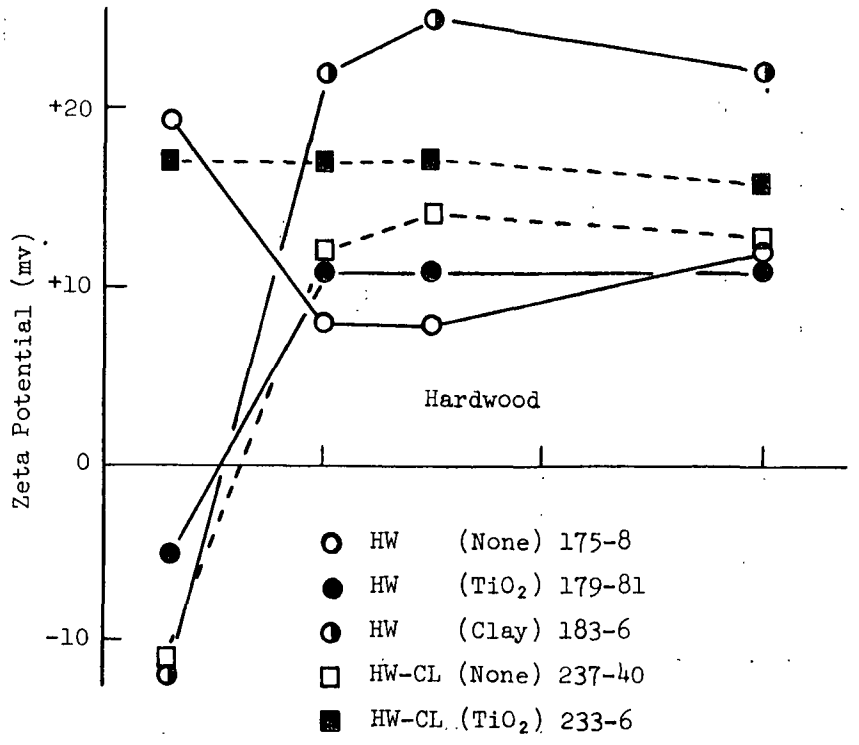


Figure 23. Zeta Potential versus Alum Concentration

which is measured. This notion is further strengthened in examining the two classified systems with TiO_2 present (solid squares). Here, where there are few fines present, the zeta potential is always positive and presumably one is measuring the zeta potential of the pigment particles.

The results of clay retention measurements in the unclassified systems is shown in Fig. 24 and the zeta potential results are also shown in Fig. 23. In essence the results are quite similar to the TiO_2 results, except for the level of the single pass retentions. For either pigment the hardwood and softwood pulps behave similarly, with retentions being slightly higher for the hardwood pulp. The retentions of either material in the groundwood system are very high, except at the lowest alum levels (where the zeta potentials are still negative).

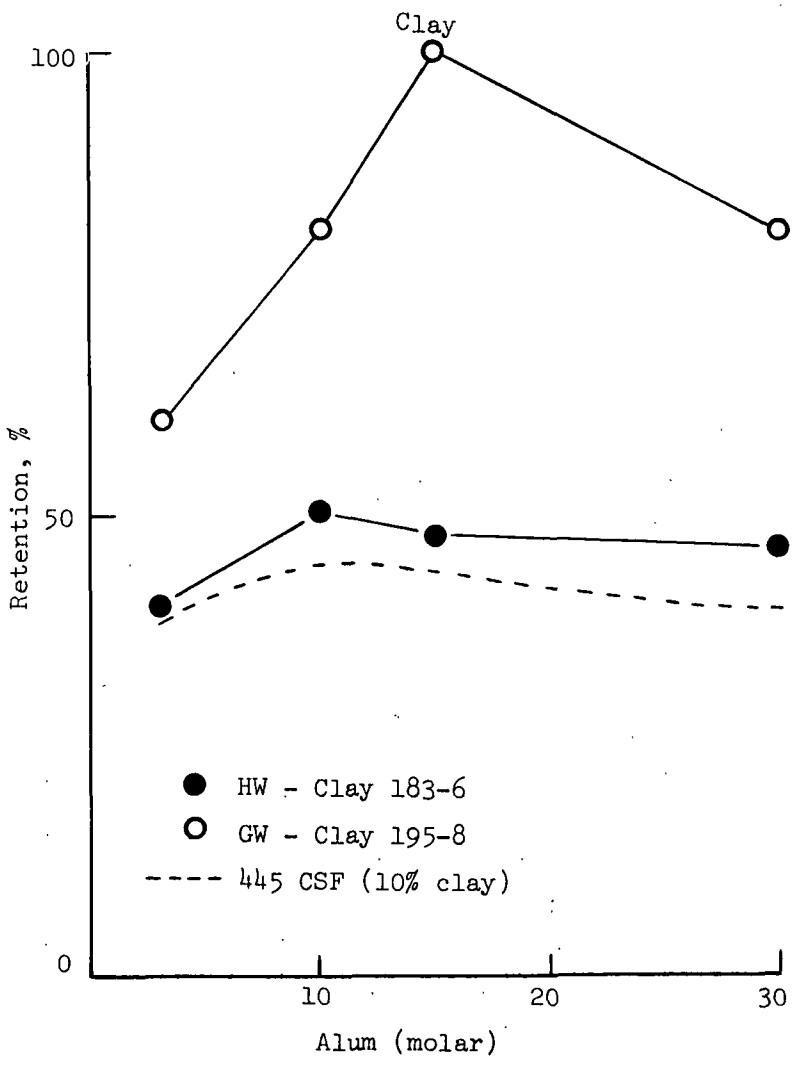


Figure 24. Single Pass Clay Retention versus Alum Concentration.

If nothing more, the retention results obtained for the six widely diverse pulp systems, when compared with the corresponding behavior of zeta potential, point out the difficulties in using the latter parameter as an indicator of the electrokinetic state of the colloidal suspension. Clearly the optimum retention does not always occur in the vicinity of zero zeta potential. However, this criterion is apparently valid in a number of the situations depicted in this report and in PR1. [In systems with polymeric retention aids the correlation is even poorer, but the zeta potential may still be a useful indicator of system changes. This latter area is part of a separate Institute project concerned with the action of polymers as retention and drainage aids, (IPC Project 3276).

The fines loss data for the HW and GW pulps with no filler, 5% TiO_2, and 10% clay are shown in Table V. In the hardwood pulp the fines loss increases in the clay and TiO_2 systems with increasing alum. This is in disagreement with the results reported for the 445 CSF pulp and classified pulp in PR1, but is consistent with the trend reported in Table II and discussed on page 6. If, as suggested there, the small increase in fines loss is an experimental artifact associated with the inability to separate aluminum absorbed on the fines, then the same trend should be evident for the experiments where no filler is present (175-178). Table V indicates that for the pulp only systems (GW and KHW) there is no dependence of fines loss on alum concentration.

As expected the fines loss in the groundwood system is greater than found for the other pulps. Furthermore the fines loss increases when filler material is present, and is about the same (4 to 5%) for either clay or TiO_2. In the clay containing system there is no apparent trend of increasing loss with increasing alum.

TABLE V

FINES LOSS (G/1000 ML)

0.3% Consistency, pH = 5.0, 70 cpm

Pulp	Data Set No.	Filler	Alum x 10^{-5}	Weight Fines	% Fine Loss	Zeta Potential, mv
Hardwood	175	None	3	0.0836	2.8	19
	176	None	10	0.0952	3.2	8
	177	None	15	0.0804	2.7	8
	178	None	30	0.0800	2.7	12
Hardwood	179	5% TiO_2	3	0.0816	2.7	-5
	180	5	10	0.0816	2.7	11
	181	5	15	0.0832	2.8	11
	182	5	30	0.0996	3.3	11
Hardwood	183	10% Clay	3	0.0776	2.6	-12
	184	10	10	0.0908	3.0	22
	185	10	15	0.0988	3.3	25
	186	10	30	0.1152	3.8	22
Groundwood	187	None	3	0.1440	4.8	5
	188	None	10	0.1040	3.5	6
	189	None	15	0.1140	3.8	2
	190	None	30	0.1124	3.7	7
Groundwood	191	5% TiO_2	3	0.1628	5.4	-7
	192	5	10	0.1430	4.8	-2
	193	5	15	0.1315	4.4	8
	194	5	30	0.1405	4.7	5
Groundwood	195	10% Clay	3	0.1612	5.3	-11
	196	10	10	0.1360	4.5	0
	197	10	15	0.1330	4.4	6
	198	10	30	0.1430	4.8	5

In an attempt to correlate retention with the amount of fines present in the original furnishes, each of four pulps were processed through a Bauer-McNett Classifier. The four pulps are the 445 CSF, Classified softwood, GW, and HW. The percent of the original material which passed through a 150 mesh screen is taken as the fines fraction of the pulp. The single pass retention values shown in Fig. 22 and 24, and Fig. 1 of PR1, have been plotted against the "fines fraction" of the pulp in Fig. 25, at an alum level of 10×10^{-5} molar. The solid lines are linear regression lines. The dependence of retention of TiO_2 or clay on the quantity of fines preent is evident. These trends are consistent with the findings of PR1, namely that the retention of clay is much more sensitive to the presence of fines than is TiO_2. Figure 25 suggests that for clay, if no fines were present in the system, the retention would be very small (10% or so). On the other hand, TiO_2 retentions with no fines present still amount to 40 to 50%. In PR1 it was noted that these larger retentions result from TiO_2 particles attached to the fineslike fibrils extending from the fiber surface. In the case of clay such associations are not observed, presumably because the larger clay particles are torn away from the fibrils by the hydrodynamic forces of mixing and drainage.

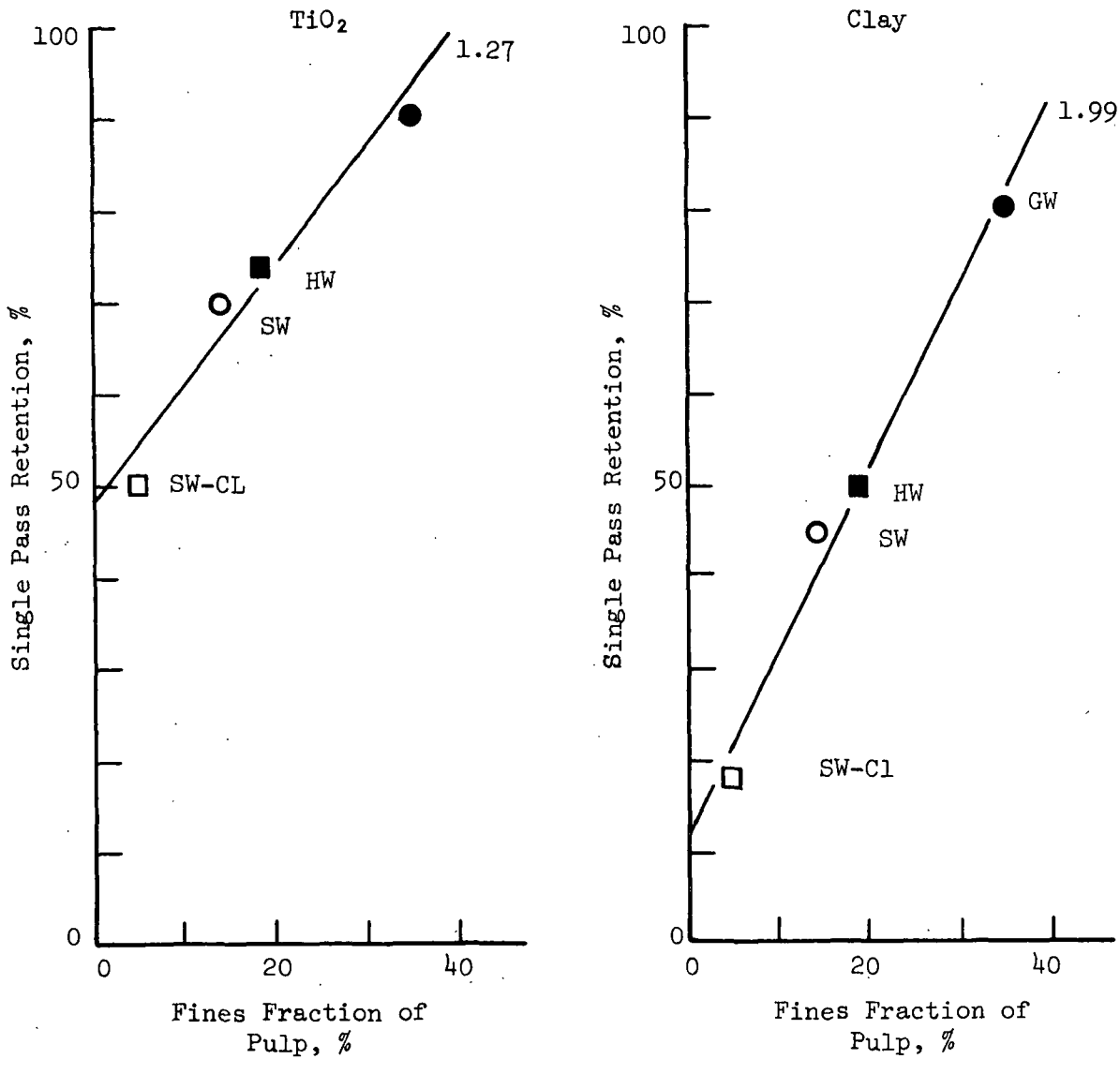


Figure 25. Single Pass Retention of Clay and TiO_2 versus Fines Fraction of the Pulp

EXPERIMENTAL

MATERIALS

Pulp

The pulps used in this portion of the work are those used in Phase I and are characterized in Progress Report One. In addition, two new pulps are examined. These include a bleached kraft hardwood pulp and a groundwood pulp. Fiber analyses showed that the hardwood pulp contained a mixture of hardwood species including maple, beech, birch, basswood, cherry and Populus. The groundwood pulp was comprised principally of spruce with a small percentage of hardwood (Populus). For our use the hardwood pulp which was received in dry lap form was refined with the use of a Valley beater. Five pound batches of the pulp were refined at 2.2% consistency in tap water to a Canadian freeness of 500 cc. The refined pulp was then dewatered, washed twice with deionized water and dewatered to 40% solids. Preservative was then added and the pulp stored under refrigeration for subsequent use. The groundwood pulp which was received in slurry form was dewatered to 25% solids, preservative added and refrigerated. The Canadian freeness of the pulp was 95 cc.

Samples of hardwood and groundwood pulps were classified to remove all fibers that would pass through a 100 mesh screen. The pulps were classified with a Bauer-McNett classifier using 20, 35, 65 and 100 mesh screens. Ten gram aliquots of pulp (o.d. basis) were classified for a period of 20 minutes using filtered tap water. The four fractions of pulp that were retained by the screens were then collected on muslin cloth, combined, washed and dewatered. The classified hardwood had a Canadian freeness of 615 cc and the classified groundwood of 705 cc.

Preparation of Hard Water

Artificial hard waters were utilized in the preparation of a number of sets of handsheets in this phase of the work. Batches of hard water were prepared by adding various analytical reagent grade chemicals to distilled water. The regular hard water which has a hardness of 435 ppm (as $CaCO_3$) contains the following chemicals in 25 liters distilled water: 2.295 g $CaSO_4 \cdot 2\ H_2O$, 9.413 g $CaCl_2 \cdot 2\ H_2O$, 3.093 g $MgSO_4$, 1.725 g $NaHCO_3$ and 9.595 g Na_2SO_4. The pH of the water was 7.4.

A modification of the regular hard water was made whereby all of the sulfate ions of the regular hard water are replaced with chloride ions while maintaining the anion content level. The chemicals added to 25 liters distilled water to obtain this hard water without sulfate ions are as follows: 11.361 g $CaCl_2 \cdot 2\ H_2O$, 5.221 g $MgCl_2 \cdot 6\ H_2O$, 1.725 g $NaHCO_3$ and 7.838 g NaCl. The pH of the water was 7.5.

A third hard water was prepared which contained 50% as many sulfate ions as the regular hard water. The following chemicals were added to 25 liters of distilled water: 2.296 g $CaSO_4 \cdot 2\ H_2O$, 3.092 g $MgSO_4$, 2.028 g Na_2SO_4, 9.412 g $CaCl_2 \cdot 2\ H_2O$ and 1.725 g $NaHCO_3$. The pH of the water was 7.2.

A fourth hard water was prepared which contained only 10% as many sulfate ions as the regular hard water. The chemicals added to 25 liters distilled water are as follows: 1.836 g $CaSO_4 \cdot 2\ H_2O$, 9.804 g $CaCl_2 \cdot 2\ H_2O$, 5.222 g $MgCl_2 \cdot 6\ H_2O$, 7.892 NaCl and 1.735 g $NaHCO_2$. The pH of this water was 7.4.

A fifth hard water was prepared in which all of the bicarbonate ions were replaced with sulfate ions. The following chemicals were added to 25 liters distilled water: 2.294 g $CaSO_4 \cdot 2\ H_2O$, 9.414 g $CaCl_2 \cdot 2\ H_2O$, 3.094 g $MgSO_4$ and 12.510 g Na_2SO_4. The pH of this water was 5.7.

Ions in the Supernatant

The amount of Al, Cu, Mg and Ca ions was determined by atomic absorption spectrometry. Aliquots of 100 ml of supernatant were acidified and evaporated down to 25 ml. All samples, standards and blanks were equated to 1000 ppm Na. The limits of detection of Al ranged from 0.10 to 0.25 ppm, for Ca 0.006 ppm, for Mg 0.16 to 0.17 and 1.74 for Ca.

The amount of SO_4 ion was determined by a turbidimetric analysis method and the amount of Cl ion determined by a mercuric nitrate method given by Standard Methods for the Examination of Water and Waste Water, 15th Edition (1971). The SO_4 ion analysis is given on page 334 and Cl ion analysis on page 97.

The amount of Na ion was determined by flame spectrometry using the DU spectrophotometer at a wavelength of 589.

Filler Materials

The same filler materials were used in this portion of the work as those used in Phase I and are described in detail in PR1.

Handsheet Preparation

The equipment and procedures employed in handsheet preparation are described in PR1. Briefly, the handsheets were prepared on an 8-inch diameter Rapid-Kothen sheet mold. For a single pass system, 10 g of pulp was dispersed at the desired consistency in water. Various additives were then introduced into

the pulp slurry and allowed to stir in five minutes apiece. The order of addition of the additives is rosin, alum, clay, TiO_2 followed by a pH adjustment. For each handsheet aliquots of pulp furnish containing 2 g of fibers were metered into the sheet mold. After the furnish was agitated for 15 seconds it was drained and a sheet formed on the wire. The wet sheet was then couched from the wire with blotters, pressed and dried. The white water contained in the leg of the mold lined with a plastic bag was removed by siphoning.

Sets of handsheets were prepared using a multicycle white water system with the white water being recycled a total of eight times. For the first cycle 36 g pulp was dispersed at 0.3% consistency in 12 liters water. Alum and filler were then added and the pH adjusted to 5. Eighteen handsheets, containing nominally 2 g fibers per sheet, were prepared from the furnish. The pulp to be used in the second cycle was dispersed in 10 liters white water obtained from the first cycle. The same amount percentagewise of alum and filler as was added in the first cycle was added in the second. The pH was then adjusted to 5. Fifteen sheets were prepared in the second cycle. For the third cycle 25 g pulp was dispersed in 8.33 liters of white water obtained from the second cycle and again alum and filler added. As in the second cycle the percentage of alum and filler added is based on the amount of fibers. Handsheets were prepared from the furnish. For the remainder of the eight cycles, the pulp furnishes and handsheets were prepared in a similar manner. In several runs, filler and/or alum was only added to the furnishes for the first four cycles. None was added in cycle 5 through 8.

The handsheet analysis, optical measurements and zeta potential measurements utilized in this portion of the work are the same as those used in Phase I and are describd in detail in PR1.

Retentions in Mixed Filler Systems

In the cases where both TiO_2 and clay were present in the handsheets the retention of TiO_2 was determined by intensity ratios using an x-ray diffraction method. The method is described in Report One. The clay retention was determined by ashing. The calculations included the total ash of the handsheets, the amount of TiO_2 retained as determined by x-ray method and the amount of ash in the control.

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3. Chen, F.-J., Unpublished work, The Institute of Paper Chemistry.

4. Project 3245, Report No. 1, Figure 8, page 24.

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APPENDIX

TABLE VI

EXPERIMENTAL CONDITIONS

pH = 5, agitation = 70 cpm

Set No.	Pulp	Alum	Filler		Rosin	Water
111	445	3 x 10^{-5}M	5% TiO_2,	25% clay	--	Distilled
112	445	10 x 10^{-5}M	"	"	--	"
113	445	15 x 10^{-5}M	"	"	--	"
114	445	30 x 10^{-5}M	"	"	--	"
115	Fines free	3 x 10^{-5}M	"	"	--	"
116	Fines free	10 x 10^{-5}M	"	"	--	"
117	Fines free	15 x 10^{-5}M	"	"	--	"
118	Fines free	30 x 10^{-5}M	"	"	--	"
119	445	3 x 10^{-5}M	"	"	2%	"
120	445	10 x 10^{-5}M	"	"	"	"
121	445	15 x 10^{-5}M	"	"	"	"
122	445	30 x 10^{-5}M	"	"	"	"
123	Fines free	3 x 10^{-5}M	"	"	"	"
124	Fines free	10 x 10^{-5}M	"	"	"	"
125	Fines free	15 x 10^{-5}M	"	"	"	"
126	Fines free	30 x 10^{-5}M	"	"	"	"
127	Fines free	30 x 10^{-5}M	--	--	"	"
128	445	30 x 10^{-5}M	--	--	--	"
129	445	3 x 10^{-5}M	5% TiO_2,	25% clay	--	Hard
130	445	10 x 10^{-5}M	"	"	--	"
131	445	15 x 10^{-5}M	"	"	--	"
132	445	30 x 10^{-5}M	"	"	--	"
133	Fines free	3 x 10^{-5}M	"	"	--	"
134	Fines free	10 x 10^{-5}M	"	"	--	"
135	Fines free	15 x 10^{-5}M	"	"	--	"
136	Fines free	30 x 10^{-5}M	"	"	--	"
137	445	30 x 10^{-5}M	--	--	--	"
138	Fines free	30 x 10^{-5}M	--	--	--	"
139	445	3 x 10^{-5}M	--	--	--	Distilled
140	445	10 x 10^{-5}M	--	--	--	"
141	445	15 x 10^{-5}M	--	--	--	"
142	445	30 x 10^{-5}M	--	--	--	"
143	Fines free	3 x 10^{-5}M	--	--	--	"
144	Fines free	10 x 10^{-5}M	--	--	--	"
145	Fines free	15 x 10^{-5}M	--	--	--	"
146	Fines free	30 x 10^{-5}M	--	--	--	"
147	445	3 x 10^{-5}M	--	--	2%	"
148	445	10 x 10^{-5}M	--	--	"	"
149	445	15 x 10^{-5}M	--	--	"	"

TABLE VI (Continued)

EXPERIMENTAL CONDITIONS

pH = 5, agitation = 70 cpm

Set No.	Pulp	Alum	Filler		Rosin	Water
150	445	30 x 10^{-5}M	--	--	2%	Distilled
151	Fines free	3 x 10^{-5}M	--	--	"	"
152	Fines free	10 x 10^{-5}M	--	--	"	"
153	Fines free	15 x 10^{-5}M	--	--	"	"
154	Fines free	30 x 10^{-5}M	--	--	"	"
155	445	3 x 10^{-5}M	--	--	--	Hard
156	445	10 x 10^{-5}M	--	--	--	"
157	445	15 x 10^{-5}M	--	--	--	"
158	445	30 x 10^{-5}M	--	--	--	"
159	Fines free	3 x 10^{-5}M	--	--	--	"
160	Fines free	10 x 10^{-5}M	--	--	--	"
161	Fines free	15 x 10^{-5}M	--	--	--	"
162	Fines free	30 x 10^{-5}M	--	--	--	"
163	445	3 x 10^{-5}M	5% TiO_2, 25% clay		2%	"
164	445	10 x 10^{-5}M	"	"	"	"
165	445	15 x 10^{-5}M	"	"	"	"
166	445	30 x 10^{-5}M	"	"	"	"
167	Fines free	3 x 10^{-5}M	"	"	"	"
168	Fines free	10 x 10^{-5}M	"	"	"	"
169	Fines free	15 x 10^{-5}M	"	"	"	"
170	Fines free	30 x 10^{-5}M	"	"	"	"
171	445 (recycle)	10 x 10^{-5}M	--	--	--	"
172[1]	445 (recycle)	10 x 10^{-5}M	--	--	--	"
173	445 (recycle)	10 x 10^{-5}M	10% clay		--	"
174	445 (recycle)	10 x 10^{-5}M	25% clay		--	"
175	Bl. hardwood kraft	3 x 10^{-5}M	--		--	Distilled
176	Bl. hardwood kraft	10 x 10^{-5}M	--		--	"
177	Bl. hardwood kraft	15 x 10^{-5}M	--		--	"
178	Bl. hardwood kraft	30 x 10^{-5}M	--		--	"
179	Bl. hardwood kraft	3 x 10^{-5}M	5% TiO_2		--	"
180	Bl. hardwood kraft	10 x 10^{-5}M	"		--	"
181	Bl. hardwood kraft	15 x 10^{-5}M	"		--	"
182	Bl. hardwood kraft	30 x 10^{-5}M	"		--	"
183	Bl. hardwood kraft	3 x 10^{-5}M	10% clay		--	"
184	Bl. hardwood kraft	10 x 10^{-5}M	"		--	"
185	Bl. hardwood kraft	15 x 10^{-5}M	"		--	"
186	Bl. hardwood kraft	30 x 10^{-5}M	"		--	"
187	Groundwood	3 x 10^{-5}M	--		--	--
188	Groundwood	10 x 10^{-5}M	--		--	--
189	Groundwood	15 x 10^{-5}M	--		--	--

[1]The agitation rate of the pulp in the sheet mold was 140 cpm.

TABLE VI (Continued)

EXPERIMENTAL CONDITIONS

pH = 5, agitation = 70 cpm

Set No.	Pulp	Alum	Filler	Rosin	Water
190	Groundwood	30 x 10^{-5}M	10% clay	--	--
191	Groundwood	3 x 10^{-5}M	5% TiO_2	--	--
192	Groundwood	10 x 10^{-5}M	--	--	--
193	Groundwood	15 x 10^{-5}M	--	--	--
194	Groundwood	30 x 10^{-5}M	--	--	--
195	Groundwood	3 x 10^{-5}M	10% clay	--	--
196	Groundwood	10 x 10^{-5}M	--	--	--
197	Groundwood	15 x 10^{-5}M	--	--	--
198	Groundwood	30 x 10^{-5}M	--	--	--
199	445	10 x 10^{-5}M	25% clay	--	Modified hard[1]
200	445 (recycle)	10 x 10^{-5}M	5% TiO_2	--	Hard
201	445	10 x 10^{-5}M	"	--	"
202	Fines free	10 x 10^{-5}M	"	--	"
203	445	10 x 10^{-5}M	"	--	Modified hard[1]
204	Fines free	10 x 10^{-5}M	"	--	"
205	445	10 x 10^{-5}M	"	--	Distilled
206	Fines free	10 x 10^{-5}M	"	--	"
207	445	10 x 10^{-5}M	--	--	Hard
208	Fines free	10 x 10^{-5}M	--	--	"
209	445	10 x 10^{-5}M	--	--	Modified hard[1]
210	Fines free	10 x 10^{-5}M	--	--	"
211	445	10 x 10^{-5}M	10% clay	--	Hard
212	445	10 x 10^{-5}M	"	--	Modified hard[1]
213	445 (recycle)	10 x 10^{-5}M	15% TiO_2[2]		Hard
214	445	--	10% clay	--	"
215	445	--	5% TiO_2	--	"
216	445	10 x 10^{-5}M	15% TiO_2	--	Modified hard[3]
217	Fines free	10 x 10^{-5}M	"	--	"
218	445	10 x 10^{-5}M	"	--	Modified hard[4]
219	Fines free	10 x 10^{-5}M	"	--	"
220	445	10 x 10^{-5}M	"	--	Modified hard[5]
221	445	10 x 10^{-5}M	"	--	Modified hard[6]
222	445 (recycle)	10 x 10^{-5}M[7]	15% TiO_2[7]		Hard
223	445 (recycle)	10 x 10^{-5}M	25% clay[8]	--	"

[1]The sulfate ions in the regular hard water have been replaced with chloride ions.
[2]The filler was added to only the first four cycles.
[3]Modified hard water diluted 1:1 with distilled water.
[4]Modified hard water diluted 9:1 with distilled water.
[5]Water containing 50% as much sulfate ions as regular hard water.
[6]Water containing 10% as much sulfate ions as regular hard water.
[7]The filler and alum were added to only the first four cycles.
[8]The filler was added to only the first four cycles.

TABLE VI (Continued)

EXPERIMENTAL CONDITIONS

pH = 5, agitation = 70 cpm

Set No.	Pulp	Alum	Filler	Rosin	Water
224	445	--	5% TiO_2	--	Hard[1]
225	445	--	"	--	Hard[2]
226	445	--	"	--	Modified hard
227	445	--	"	--	Modified hard[3]
228	445	--	"	--	Modified hard[4]
229	445	10 x 10^{-5}M	15% TiO_2	--	Hard[5]
230	445	10 x 10^{-5}M	"	--	Hard[5,6]
231	445	10 x 10^{-5}M	"	--	Modified hard
232	445	10 x 10^{-5}M	"	--	Modified hard[3]
233	Classified hardwood	3 x 10^{-5}M	5% TiO_2	--	Distilled
234	Classified hardwood	10 x 10^{-5}M	"	--	"
235	Classified hardwood	15 x 10^{-5}M	"	--	"
236	Classified hardwood	30 x 10^{-5}M	"	--	"
237	Classified hardwood	3 x 10^{-5}M	--	--	"
238	Classified hardwood	10 x 10^{-5}M	--	--	"
239	Classified hardwood	15 x 10^{-5}M	--	--	"
240	Classified hardwood	30 x 10^{-5}M	--	--	"
241	Classified groundwood	3 x 10^{-5}M	5% TiO_2	--	"
242	Classified groundwood	10 x 10^{-5}M	"	--	"
243	Classified groundwood	15 x 10^{-5}M	"	--	"
244	Classified groundwood	30 x 10^{-5}M	"	--	"
245	Classified groundwood	3 x 10^{-5}M	--	--	"
246	Classified groundwood	10 x 10^{-5}M	--	--	"
247	Classified groundwood	15 x 10^{-5}M	--	--	"
248	Classified groundwood	30 x 10^{-5}M	--	--	"

[1]Hard water diluted 1:1 with distilled water.
[2]Hard water diluted 9:1 with distilled water.
[3]Modified hard water diluted 1:1 with distilled water.
[4]Modified hard water diluted 9:1 with distilled water.
[5]The sulfate ions in the regular hard water have been replaced with bicarbonate ions.
[6]The pH of the furnish was adjusted to 5 before adding the TiO_2.